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CLAIMS

[Claim(s)]

[Claim 1] The anionic or cationic ink containing the solvent which dissolves color material, the polymerization nature component converted into a polymer by grant of energy, and this polymerization nature component, and the above-mentioned ink are an ink set characterized by combining the liquid constituent which contains in reversed polarity the particle to which the front face is charged in the state of distribution.

[Claim 2] The ink set according to claim 1 whose energy to give is ultraviolet rays, an electron ray, or heat.

[Claim 3] Furthermore, the ink set according to claim 1 which contains a photopolymerization initiator in a liquid constituent and/or ink.

[Claim 4] The ink set according to claim 1 constituted preventing condensation of the color material in ink in case a particle forms the coloring section on recorded media so that this particle front face may be adsorbed in color material.

[Claim 5] The ink set according to claim 1 with which the color material in ink is constituted by the front face so that it may adsorb in the state of a single molecule in case a particle forms the coloring section on recorded media.

[Claim 6] The ink set according to claim 1 whose ink is at least one chosen from yellow ink, Magenta ink, cyanogen ink, black ink, red ink, blue ink, and Green ink.

[Claim 7] The ink set according to claim 1 whose ink is in a separate condition respectively and contains yellow ink, Magenta ink, and cyanogen ink.

[Claim 8] The ink set according to claim 1 whose ink is in a separate condition respectively and contains yellow ink, Magenta ink, cyanogen ink, and black ink.

[Claim 9] The ink set according to claim 1 in the range whose ink is anionic and whose F-potential of a liquid constituent is +5—+90mV.

[Claim 10] The ink set according to claim 1 with which ink is anionic and pH of this liquid constituent is adjusted for the liquid constituent to 2-7 including the acid.

[Claim 11] The ink set according to claim 10 whose underwater primary dissociation constant electric dissociation exponent of an acid is five or less.

[Claim 12] An ink set given in any 1 term of claims 1-11 which ink has anionic and the anionic compound contains in ink.

[Claim 13] The ink set containing the water soluble dye which has an anionic radical as an anionic compound according to claim 12.

[Claim 14] The ink set containing the pigment which has an anionic radical on a front face as an anionic compound according to claim 12.

[Claim 15] The ink set according to claim 12 whose ink contains a pigment and the anionic compound which is the dispersant of this pigment.

[Claim 16] The ink set according to claim 1 in the range whose ink is cationicity and whose F-potential of a liquid constituent is -5—90mV.

[Claim 17] The ink set according to claim 1 with which ink is cationicity and pH of this liquid constituent is adjusted for the liquid constituent to the range of 7-12 including the base.

[Claim 18] The ink set according to claim 17 whose underwater primary dissociation constant

pKb of a base is five or less.

[Claim 19] An ink set given in any 1 term of claims 1-8 which ink has cationicity and the cationic compound contains in this ink, and claims 16-18.

[Claim 20] An ink set given in any 1 term of claims 1-19 in the range whose mean particle diameter of a particle is 0.005-1 micrometer.

[Claim 21] (i) The process which gives the anionic or cationic ink containing the solvent which dissolves the polymerization nature component and this polymerization nature component which carry out a polymerization to color material by grant of energy to recorded media, And it is the approach of forming the coloring section in the recorded media which have the process which gives the liquid constituent which contains in a polarity contrary to (ii) this ink the particle to which the front face is charged in the state of distribution to recorded media. The formation approach of the coloring section to the recorded media characterized by being given so that the above-mentioned ink and a liquid constituent may touch the front face of the above-mentioned recorded media in the state of a liquid mutually.

[Claim 22] The formation approach of the coloring section to the recorded media according to claim 21 with which a process (i) is performed after a process (ii) is performed at least.

[Claim 23] The formation approach of the coloring section to the recorded media according to claim 21 with which a process (ii) is performed after a process (i) is performed at least.

[Claim 24] The formation approach of the coloring section to the recorded media according to claim 21 constituted so that a process (ii) may be performed after a process (i) is performed, and a process (i) may be performed again after that.

[Claim 25] The formation approach of the coloring section to recorded media given in any 1 term of claims 21-24 which perform grant to the recorded media of the ink in a process (i) by the ink jet record approach of a method of making this ink breathing out from an orifice according to a record signal.

[Claim 26] The formation approach of the coloring section to the recorded media according to claim 25 whose ink jet record approach is an approach of making ink breathing out from an orifice by making heat energy acting on ink.

[Claim 27] The formation approach of the coloring section to recorded media given in any 1 term of claims 21-26 which perform grant to the recorded media of the liquid constituent in a process (ii) by the ink jet record approach of a method of making this liquid constituent breathing out from an orifice according to a record signal.

[Claim 28] The formation approach of the coloring section to the recorded media according to claim 27 whose ink jet record approach is an approach of making heat energy acting on a liquid constituent, and making a liquid constituent breathing out from an orifice.

[Claim 29] The formation approach of the coloring section to the recorded media characterized by performing the process which gives energy and carries out the polymerization of this polymerization nature component after forming the coloring section in any 1 term of claims 21-28 by the approach of a publication.

[Claim 30] The formation approach of the coloring section to the recorded media according to claim 29 whose energy to give is ultraviolet rays, an electron ray, or heat.

[Claim 31] The ink hold section which held the anionic or cationic ink containing the solvent which dissolves the polymerization nature component and this polymerization nature component which carry out a polymerization to color material by grant of energy, The 1st record unit equipped with the ink jet head for making this ink breathe out, The liquid constituent hold section which held the liquid constituent which contains in a polarity contrary to the above-mentioned ink the particle to which the front face is charged in the state of distribution, The ink jet recording device characterized by having the 2nd record unit equipped with the ink jet head for making this liquid constituent breathe out, and the means which carries out the polymerization of this polymerization nature component.

[Claim 32] The ink hold section which held the anionic or cationic ink containing the solvent which dissolves color material, the polymerization nature component converted into a polymer by grant of energy, and this polymerization nature component, The liquid constituent hold section which held the liquid constituent which contains in a polarity contrary to this ink the particle to

which the front face is charged in the state of distribution, The ink jet recording device characterized by having the ink jet head for making the ink held in the above-mentioned ink hold section, and the liquid constituent held in the above-mentioned liquid constituent hold section breathe out independently respectively, and the means which carries out the polymerization of this polymerization nature component.

[Claim 33] The ink jet recording device according to claim 31 or 32 whose ink jet head is a thermal ink jet head which makes heat energy act and makes a liquid breathe out.

[Claim 34] The formation approach of the coloring section to the recorded media according to claim 29 whose energy to give is ultraviolet rays, an electron ray, or heat.

[Claim 35] It is given to recorded media with the anionic or cationic ink containing the solvent which dissolves the polymerization nature component and this polymerization nature component which carry out a polymerization to color material by grant of energy. It is a liquid constituent containing the particle used for forming the coloring section on these recorded media. The liquid constituent characterized by adsorbing or joining together and making it, formation of the above-mentioned coloring section holding an equivalent molecule condition substantially with the molecule condition which the above-mentioned liquid constituent and the above-mentioned ink contact in the state of a liquid, and the color material in ink has in ink on the particle front face of a liquid constituent.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About the technique of obtaining the image which was excellent in color enhancement and the homogeneity of a color in formation of a color picture, this invention is divided and relates to the approach and ink jet recording device which form the coloring section in the ink set using the liquid constituent and this which can be used using an ink jet recording method the the best for the image formation to the absorbency scarce recorded media of the art paper for printing, a plastics, a metal, etc., etc., and recorded media.

[0002]

[Description of the Prior Art] The ink jet record approach makes ink fly, and records by making ink adhere to recorded media, such as paper. For example, according to the ink jet record approach of a method of making a drop breathing out by giving heat energy to ink and generating air bubbles, using an electric conversion object as a regurgitation energy supply means currently indicated in JP,61-59911,B, JP,61-59912,B, and JP,61-59914,B, high density multi-orifice-ization of a recording head can be realized easily, and high resolution and a high-definition image can be recorded at high speed.

[0003] By the way, as for the ink used for the conventional ink jet record approach, what uses water as a principal component and contains water-soluble high boilers, such as a glycol, for the purpose, such as desiccation prevention of the ink within a nozzle and blinding prevention of a nozzle, in this is common. Therefore, when it records on recorded media using such ink, problems, such as generating of the ununiformity image presumed not to acquire fixable [sufficient] or to be based on uneven distribution of the loading material in the recording paper front face as recorded media and a sizing compound, may be produced.

[0004] On the other hand, the demand which searches for image quality with high film photo and this level is strong also to the ink jet record object in recent years, and the technical demand to raising the image concentration of an ink jet record image, extending a color reproduction field, and raising the homogeneity of the color of a record object further is very high.

[0005] In order to plan stabilization of the ink jet record approach, and upgrading of the record object by the ink jet record approach under such circumstances, various proposals have been made until now. the porosity particle which the approach of carrying out coating of a filler or the sizing compound is proposed on the base paper front face of recorded media as one of the proposals about recorded media, for example, adsorbs color material as a filler — a base paper — coating — carrying out — this porosity particle — the technique which forms an ink absorbing layer is indicated. The coat paper for ink jets etc. is put on the market as recorded media using these techniques.

[0006] In order to plan stabilization of the ink jet record approach, and upgrading of the record object by the ink jet record approach under such circumstances, various proposals have been made until now. Some of the typical thing is summarized to below.

(1) How to carry out internal [of a volatile solvent or the osmosis solvent] to ink : the approach of adding the compound which raises the permeability of a surfactant etc. to JP,55-65269,A into ink as a means which brings forward fixable [of the ink to recorded media] is indicated.

Moreover, using for JP,55-66976,A the ink which made the volatile solvent the subject is indicated.

(2) How to mix ink and the liquid constituent which reacts on recorded media in ink : the approach of giving the liquid constituent which cheats out of an image good on recorded media after injection in advance of improvement in image concentration, waterproof improvement, and injection of the ink for forming a record image for the purpose of control of bleeding further is proposed.

[0007] for example, to JP,63-60783,A After making the liquid constituent containing a basic polymer adhere to recorded media, the approach of recording in the ink containing an anion color is indicated. To JP,63-22681,A The record approach which mixes the second liquid constituent containing the compound which causes the 1st liquid constituent, these reactant chemical species, and reaction including reactant chemical species on recorded media is indicated. Furthermore, after giving the liquid constituent containing the organic compound which has two or more cationic radicals per molecule on recorded media, the approach of recording in the ink containing an anion color is indicated by JP,63-299971,A. Moreover, after giving the acid liquid constituent containing a succinic acid etc. on recorded media, the approach of recording in the ink containing an anion color is indicated by JP,64-9279,A.

[0008] Furthermore, the method of using the liquid constituent with which the method of giving the liquid constituent which makes JP,64-63185,A insolubilize a color to paper in advance of grant of ink contains in JP,8-224955,A the cationic matter with which molecular-weight-distribution fields differ with the ink containing an anionic compound is indicated, and the method of using the cationic matter and the liquid constituent containing a pulverizing cellulose for JP,8-72393,A with ink is indicated, respectively.

[0009] In these open official reports, image concentration is all high, printing grace and a water resisting property are good in them, and it is indicated that a good image is obtained also in color reproduction nature and bleeding. Furthermore, after recording in color ink on recorded media, the approach of giving the deck-watertight-luminaire-ized agent which forms a color and a lake is indicated by JP,55-150396,A, and giving the water resisting property of a record image is proposed.

[0010] How to mix ink and a particle content liquid constituent on recorded media : (3) To JP,4-259590,A After giving the colorless liquid containing the colorless particle which consists of mineral matter on recorded media, the approach to which nonaqueous recording ink is made to adhere is indicated. To JP,6-92010,A After giving the solution containing the solution containing a particle or a particle, and a binder polymer on recorded media, The approach to which the ink containing a pigment, water soluble resin, a water soluble solvent, and water is made to adhere is indicated. It is indicated that the record ingredient which contains in JP,2000-34432,A the liquid constituent which consists of a water-insoluble nature particle, and ink is indicated, and depend neither on a paper type, but printing grace and a color-enhancing good image are obtained.

[0011] Moreover, the solid ink injected and printed from a head by one side where it dissolved the color in the wax system constituent solidified in ordinary temperature as an approach of carrying out image formation to absorbency to a scarce base material conventionally and heating fusion is carried out is known. Furthermore, the thing using ultraviolet curing mold resin as the image formation approach to a plastic plate is indicated by JP,63-235382,A, JP,3-43292,A, JP,60-27589,B, JP,5-64667,B, JP,5-186725,A, JP,7-224241,A, JP,8-150707,A, JP,8-218018,A, etc.

[0012] (Background technique) Although this invention persons could check the effectiveness which was excellent to each technical technical problem as a result of repeating examination about various kinds of ink jet record techniques which were described above, they found out that other ink jet recording characteristics may fall in exchange for it. For example, the recorded media (it is henceforth called coat paper) obtained by carrying out coating of a filler or the sizing compound on the base paper front face of the above-mentioned recorded media are recognized as a technique which can form a quality image.

[0013] Generally, in order to obtain the image of high saturation, it is known that it is required to leave on the surface of recorded media in the state of a single molecule, without making color

material condense. There is such a function in the porosity particle of coat paper. However, in order to obtain high image concentration and image saturation, formation of a thick ink absorbing layer which covers a base paper by a lot of porosity particles becomes indispensable to the color material in the given ink, and there is a problem that the texture of a base paper will be lost, as a result. The thing whose ink absorbing layer to the extent that this invention persons lose the texture of a base paper in this way is the need surmised that color material originated in not sticking to a porosity particle efficiently.

[0014] The conventional coat paper is explained below supposing the coat paper which has much more ink absorbing layer. Drawing 5 shows typically the cross section near a coat paper front face. In this drawing, 501 is a base paper and 503 shows an ink absorbing layer. Generally, an ink absorbing layer 503 has the adhesives 507 which fix the porosity particle 505 and them. If ink is given, ink will permeate the opening between the porosity particles 505 according to capillarity, and will form the ink osmosis section 505. Like, since [which was shown in this drawing] the porosity particles in an ink absorbing layer differ in a consistency locally, the method of osmosis of the ink by this capillarity changes with locations. For this reason, in the osmosis process of ink, color material cannot contact homogeneity on a porosity particle front face, and is not efficiently adsorbed by the porosity particle in color material.

[0015] Furthermore, the part from which osmosis of ink is prevented is also produced with adhesives 507, the part which ink cannot permeate exists in an ink absorbing layer 503, and the part which does not contribute occurs in coloring. That is, in order to be unable to adsorb color material in the state of a single molecule efficiently to the amount of a porosity particle, consequently to obtain the image of high quality for the above reasons, a lot of porosity particles were needed, and the texture of a base paper was to be spoiled in the conventional coat paper.

[0016] Moreover, by adopting the technique of the above (1), although fixable [to the recorded media of ink] improved, there was a case where the color reproduction range made important for the fall of image concentration, record in a regular paper, or record of a color picture fell. Moreover, according to the technique of the above (2), since the color material in ink can be stopped on a recorded-media front face, the record object of high image concentration can be obtained. However, probably because it was making color material condense on the surface of recorded media, there was a case where the reappearance range or saturation of a color were not fully obtained. moreover — although reforming of the surface state of recorded media was obtained by grant of the solution containing a particle with the conventional technique explained above (3) — coat paper and equivalent level — high — the brilliance image was not obtained. Especially, about nonaqueous recording ink, there is also a limit of the selectivity of color material, the record grant approach, etc., and a technical problem remains in the degree of freedom.

[0017] Moreover, there were the following problems to the case where it is the quality of the material of absorbency scarce art paper for printing with which recorded media have not performed surface preparation, such as an ink absorbing layer like coat paper, a plastics, a metal, etc., etc.

1. When using the solvent permeability to paper and using plastics etc. as a recorded material, while drainage system ink requires time amount by desiccation of ink, it cannot form an image with abrasion resistance. Therefore, the recorded media which prepared the ink absorbing layer on base materials, such as what has absorptivity like paper as recorded media, and plastics, are applicable. Moreover, in JP,8-150707,A, the liquid which has ink permeability and adhesion beforehand is recorded on the image formation section in an ink jet, and the acceptance layer is formed. However, it will be necessary to form a thick acceptance layer like the above-mentioned coat paper, and by this approach, in order to obtain the image which has sufficient color enhancement, there is a problem for which acceptance layer coating liquid is needed in large quantities. Moreover, the reinforcement of the coloring section might not fully be obtained, either.

[0018] 2. In solid ink, especially recorded media can be applied without being restricted, but since it is the soft quality of the material of a wax, a printing dot will separate easily also in weak frictional force.

3. It is necessary to heat recorded media at 120 degrees C - 180 degrees C, and recorded media are restricted about the ink of JP,60-27589,B using the sublimability color as a color material.

4. although image formation which was excellent in weatherability or scratch-proof nature on base materials, such as plastics, was made possible by the ink jet record approach by combination with the color material and ultraviolet curing mold resin which have so far been indicated — recorded media, such as a photograph paper for ink jet record in recent years, and a photograph film, — comparing — the color enhancement of a record image — going berserk — etc. — it was not enough.

[0019]

[Problem(s) to be Solved by the Invention] Thus, since the technical problem is left behind to the conventional approach by each, to much more high-definition ink jet record object, this invention persons came to have recognition that a new ink jet record technique needs to be developed in it rather than it asks in recent years. Based on the above-mentioned new knowledge, it succeeds in this invention. Namely, in order for this invention persons to adsorb or combine color material with this particle efficiently based on the above new knowledge, using the particle which has the operation which adsorbs color material By distributing this particle and using in the state of a liquid with ink, it becomes possible to make color material and a particle react by liquid-liquefied voice, and it came to succeed that the concentration and saturation of an image, weatherability, and scratch-proof nature can be raised with sufficient dependability as the result in a header and this invention.

[0020] Therefore, the purpose of this invention has the still larger color reproduction range. (The purpose of this invention) While offering the liquid constituent used in order to obtain the quality ink jet record object excellent also in the homogeneity of a color on absorbency scarce recorded media It excels in weatherability or scratch-proof nature, a record object is given, and it is in offering the dependability in printing, and the liquid constituent which is specifically excellent also in preservation stability and regurgitation stability from a recording head.

[0021] moreover, other purposes of this invention have the still larger color reproduction range, be excellent also in the homogeneity of a color, and they be in the point of offer the approach of form in recorded media the coloring section which be excellent also in the dependability in printing while there be still less stripe nonuniformity of the solid section and they can form the outstanding ink jet record object equipped also with good weatherability or scratch-proof nature on absorbency scarce recorded media.

[0022] Moreover, other purposes of this invention have the still wider color reproduction range, and it excels also in the homogeneity of a color. While generating of the stripe nonuniformity of the solid section can form the ink jet record object excellent also in the weatherability controlled by the good condition or scratch-proof nature on absorbency scarce recorded media It is in offering the ink set which combined the liquid constituent which is excellent also in the dependability in printing, and this liquid constituent, and an ink jet recording device.

[0023]

[Means for Solving the Problem] Following this invention can attain the above-mentioned purpose. That is, this invention offers the ink set characterized by the anionic or cationic ink containing the solvent which dissolves color material, the polymerization nature component converted into a polymer by grant of energy, and this polymerization nature component, and the above-mentioned ink combining the liquid constituent which contains in reversed polarity the particle to which the front face is charged in the state of distribution.

[0024] Moreover, the above-mentioned ink set whose energy which gives this invention is ultraviolet rays, an electron ray, or heat; the above-mentioned ink set; particle which contains a photopolymerization initiator in a liquid constituent and/or ink further Preventing condensation of the color material in ink, in case the coloring section is formed on recorded media The above-mentioned ink set constituted so that this particle front face may be adsorbed in color material; a particle The above-mentioned ink set with which the color material in ink is constituted by the front face so that it may adsorb in the state of a single molecule in case the coloring section is formed on recorded media; ink Yellow ink, Magenta ink, cyanogen ink, black ink, The above-mentioned ink set which is at least one chosen from red ink, blue ink, and Green ink; ink The

above-mentioned ink set which contains respectively yellow ink, Magenta ink, and cyanogen ink in the separate condition; ink offers the above-mentioned ink set which contains respectively yellow ink, Magenta ink, cyanogen ink, and black ink in the separate condition.

[0025] Moreover, the above-mentioned ink set which this invention has in the range whose ink is anionic and, whose F-potential of a liquid constituent is +5—+90mV; Ink is anionic. And the above-mentioned ink set whose primary dissociation constant electric dissociation exponent of an ink set; acid underwater [of the above by which pH of this liquid constituent is adjusted for the liquid constituent to 2–7 including the acid] is five or less; Ink has anionic. Ink And the above-mentioned ink set containing the pigment which has an anionic radical on a front face as the above-mentioned ink set; anionic compound which contains in ink the water soluble dye which has an anionic radical as the above-mentioned ink set; anionic compound which the anionic compound contains; A pigment, The above-mentioned ink set containing the anionic compound which is the dispersant of this pigment; Ink is cationicity. And the above-mentioned ink set in the range whose F-potential of a liquid constituent is –5—90mV; Ink is cationicity. And the above-mentioned ink set whose primary dissociation constant pKb of an ink set; base underwater [of the above by which pH of this liquid constituent is adjusted for the liquid constituent to the range of 7–12 including the base] is five or less; Ink has cationicity. And the above-mentioned ink set which the cationic compound contains in this ink; the above-mentioned ink set in the range whose mean particle diameter of a particle is 0.005–1 micrometer is offered.

[0026] Moreover, the process which gives the anionic or cationic ink containing the solvent which dissolves the polymerization nature component and this polymerization nature component which carry out the polymerization of this invention to (i) color material by grant of energy to recorded media, And it is the approach of forming the coloring section in the recorded media which have the process which gives the liquid constituent which contains in a polarity contrary to (ii) this ink the particle to which the front face is charged in the state of distribution to recorded media. The formation approach of the coloring section to the recorded media characterized by being given so that the above-mentioned ink and a liquid constituent may touch the front face of the above-mentioned recorded media in the state of a liquid mutually is offered.

[0027] Moreover, the formation approach of the above-mentioned coloring section that a process (i) is performed after, as for this invention, a process (ii) is performed at least; after a process (i) is performed at least The formation approach of the above-mentioned coloring section that a process (ii) is performed; after a process (i) is performed The formation approach of the above-mentioned coloring section constituted so that a process (ii) may be performed and a process (i) may be performed again after that; the grant to the recorded media of the ink in a process (i) The formation approach of the above-mentioned coloring section performed by the ink jet record approach of a method of making this ink breathing out from an orifice according to a record signal; the ink jet record approach The formation approach of the above-mentioned coloring section which is the approach of making ink breathing out from an orifice by making heat energy acting on ink; the grant to the recorded media of the liquid constituent in a process (ii) The formation approach of the above-mentioned coloring section performed by the ink jet record approach of a method of making this liquid constituent breathing out from an orifice according to a record signal; the ink jet record approach After forming the coloring section by the approach more than formation approach; of the above-mentioned coloring section which is the approach of making heat energy acting on a liquid constituent, and making a liquid constituent breathing out from an orifice, The formation approach of the above-mentioned coloring section which performs the process which gives energy and carries out the polymerization of this polymerization nature component; the formation approach of the above-mentioned coloring section that the energy to give is ultraviolet rays, an electron ray, or heat is offered.

[0028] Moreover, the ink hold section which held the anionic or cationic ink containing the solvent which dissolves the polymerization nature component and this polymerization nature component which carry out the polymerization of this invention to color material by grant of energy, The 1st record unit equipped with the ink jet head for making this ink breathe out, The liquid constituent hold section which held the liquid constituent which contains in a polarity

contrary to the above-mentioned ink the particle to which the front face is charged in the state of distribution, The ink jet recording device characterized by having the 2nd record unit equipped with the ink jet head for making this liquid constituent breathe out and the means which carries out the polymerization of this polymerization nature component is offered.

[0029] Moreover, the ink hold section which held the anionic or cationic ink containing the solvent in which this invention dissolves color material, the polymerization nature component converted into a polymer by grant of energy, and this polymerization nature component, The liquid constituent hold section which held the liquid constituent which contains in a polarity contrary to this ink the particle to which the front face is charged in the state of distribution, The ink jet head for making the ink held in the above-mentioned ink hold section, and the liquid constituent held in the above-mentioned liquid constituent hold section breathe out independently respectively, The ink jet recording apparatus characterized by having the means which carries out the polymerization of this polymerization nature component; an ink jet head The above-mentioned ink jet recording apparatus which is the thermal ink jet head which makes heat energy act and makes a liquid breathe out; the above-mentioned ink jet recording apparatus whose energy to give is ultraviolet rays, an electron ray, or heat is offered.

[0030] Moreover, this invention is given to recorded media with the anionic or cationic ink containing the solvent which dissolves the polymerization nature component and this polymerization nature component which carry out a polymerization to color material by grant of energy. It is a liquid constituent containing the particle used for forming the coloring section on these recorded media. The above-mentioned liquid constituent and the above-mentioned ink contact [formation of the above-mentioned coloring section] in the state of a liquid. And the liquid constituent characterized by being adsorbed, or joined together and made on it, the color material in ink holding an equivalent molecule condition substantially on the particle front face of a liquid constituent with the molecule condition which it has in ink is offered.

[0031]

[Embodiment of the Invention] Next, the gestalt of desirable operation is mentioned and this invention is explained in more detail. As a desirable embodiment of the approach of forming the coloring section in the recorded media of this invention (i) The process which gives the ink containing the color material of above-mentioned this invention etc. to recorded media, And it has the process which gives the liquid constituent of (ii) above-mentioned this invention to recorded media. And after constituting on the front face of the above-mentioned recorded media so that ink and a liquid constituent may touch in the state of a liquid mutually and it may be given, and forming the coloring section in it, the mode which gives energy and converts a polymerization nature component (a monomer may be called below) into a polymer is mentioned. By adopting this embodiment, it has a still larger color reproduction field, and excels also in the homogeneity of a color, and there is still less stripe nonuniformity of the solid section, and the ink jet record object equipped also with good weatherability or scratch-proof nature is stabilized on absorbency scarce recorded media, and it is obtained. Moreover, as the ink used for record and the liquid constituent itself were described above, since the configuration is very simple, the effectiveness that ink jet record of high quality and high-reliability can be performed is acquired.

[0032] (Explanation of a mechanism) Although the reason outstanding effectiveness which was described above by this invention is done so is not clear, this invention persons think that it is based on the following reasons. First, the mechanism of the record in this invention is explained according to drawing 6 and drawing 7 . In addition, the case where absorbency very scarce plastics is used for coincidence as recorded media as a liquid constituent using the water liquid constituent which contains the particle to which the front face is charged in cationicity in the state of distribution using the water color ink containing the polymerization nature component (monomer) converted into a polymer by the water soluble dye (anionic color) which has an anionic radical as ink, and energy grant is explained here.

[0033] Below, the record image concerning this invention is explained using drawing 6 . First, language is defined in advance of explanation. Setting to this invention, the "single molecule condition" has pointed out that color material, such as a color and a pigment, is maintaining mostly the condition of having dissolved or distributed in ink. If it is the range to which saturation

does not fall even if color material causes some condensation at this time, suppose that it is contained in this "single molecule condition." For example, since it is thought that it is desirable that it is a single molecule in the case of a color, suppose that it is called a "single molecule condition" also about color material other than a color for convenience. Moreover, in this invention, "the reaction of color material and a particle" shall mean the interaction of both ion-association besides both covalent bond, physical / chemical adsorption, absorption, adhesion, and others.

[0034] Drawing 6 is drawing having shown typically the condition that the coloring section I of the record image concerning this invention consisted of the main image section IM and its periphery IS. In drawing 6, the particle by which recorded media stick to 601 and color material 605 sticks to 603 chemically is shown typically. As shown in drawing 6, energy is given to the aggregate 607 and monomer of the particle 603 from which color material 605 stuck to homogeneity on the front face in the condition (it abbreviates to a "single molecule condition" henceforth) near a single molecule or a single molecule, and the particle holding the single molecule condition of color material, and the main image section IM is constituted from the ink jet record image of this invention by a polymerization and the three-dimensions crosslinked polymer 602 constructed for which the bridge and formed.

[0035] 609 is the aggregate of the particles which exist near the recorded-media front face in the main image section IM. The main image section IM is formed in a recorded-media front face of the process in which the process in which it adsorbs physically [a particle 603] or chemically, and color material 605 and a particle 603 adsorb by liquid-liquefied voice, and the process in which the whole coloring section I is stuck to solidification and recorded media by the three-dimensions crosslinked polymer which the monomer converted by energy grant. Therefore, the image formation excellent in weatherability or scratch-proof nature becomes it is rare to spoil the coloring property of the color material itself, and also in absorbency scarce record media, such as a plastics metallurgy group, image concentration and saturation are high, and the color reproduction range is wide as much as coat paper, and possible. Since the color material 605 for which the particle front face 603 was not adsorbed but which remained into ink on the other hand is diffused in a longitudinal direction to recorded media 601, it forms a very small blot in Periphery IS by color material 605 and the three-dimensions crosslinked polymer 602 which the monomer converted. Thus, in order for color material to remain near the front face of a record medium 601 and to make a very small blot of ink form in a periphery, also in an image field with many amounts of ink grants, such as the shadow section and the solid section, white MOYA and color nonuniformity are excellent in the homogeneity of a color few.

[0036] Furthermore, when the liquid constituent of this invention is used, in case the particle aggregate 609 which exists near the front face of recorded media is formed, the pore of a certain amount of magnitude is formed in the interior of an aggregate. The color material 605 which existed independently in the above-mentioned ink can permeate the interior of pore of the particle aggregate 609, and it can stick to it in the state of a single molecule ideal for near an inlet port and the wall of pore, and it can make color material remain near the front face of recorded media in more ideal condition. The color-enhancing record object which was further excellent with this can be obtained.

[0037] Drawing 7 (1) - (5) is an outline process Fig. of the approach of forming the coloring section in the recorded media concerning this invention which explains like the outline sectional view and its formation fault of the coloring section [like] 700 1 operative condition. In drawing 7, 701 is a part (it abbreviates to the "reaction section" henceforth) which mainly contains the reactant of ink and a liquid constituent, for example, the reactant of color material and a particle, and is a part equivalent to the main image section IM of drawing 6. The ink which did not participate in a reaction with the particle in a liquid constituent substantially is the part (it abbreviates to the "ink outflow section" henceforth) formed by flowing into the verge of the reaction section 701, and 702 is equivalent to the periphery IS of drawing 6 R> 6. This coloring section 700 is the following, and is made and formed.

[0038] First, the color material 704 in ink and the liquid constituent 706 which has reactivity are given to recorded media 703 as a drop (drawing 7 (1)), consequently ***** 707 of a liquid

constituent is formed (drawing 7 (2)). Within this ***** 707, it sticks to the particle 709 near the recorded-media front face physically on the surface of recorded media, or chemically. At this time, it is thought that there are some which a distributed condition becomes unstable and form the aggregate 711 of particles. On the other hand, in the part separated from the interface with the recorded media in ***** 707, it is thought that the particle 709 is maintaining the distributed condition of a basis.

[0039] Subsequently, ink 713 is given to recorded media 703 as a drop (drawing 7 (2)).

Consequently, in the interface of ink 713 and ***** 707, color material 704 sticks to a particle 709 chemically first. Since this reaction is a reaction (liquid-liquid reaction) of liquid, color material 704 is in a single molecule condition, and it is thought that it sticks to homogeneity on the front face of a particle 709. That is, on a particle front face, even if color material does not cause condensation or they condense it, they are conjectured to be small. Consequently, many particles by which the surface section of the reaction section 701 was adsorbed in color material 704 in the state of the single molecule are formed, since color material can be made to remain in the state of a single molecule in the coloring section which affects coloring most, it is high image concentration and the high record image of saturation is formed.

[0040] Subsequently, it is thought that the particle to which these color material 704 stuck is condensed by particles since a distributed condition becomes unstable. That is, the aggregate 715 formed here holds the color material of a single molecule condition also to the interior. High image concentration and the record image of high saturation are formed of this aggregate 715.

[0041] Furthermore, a part of unreacted color material 704 diffuses the inside of ***** 707, and it sticks to the front face of the unreacted particle 709. Thus, since the reaction of color material and a particle advances further in the ***** 707 interior, an image with high saturation is formed more by high concentration. And since recorded media 703 are very deficient in absorbency, the contact probability of color material 704 and a particle 709 is raised, a reaction comparatively uniformly and fully advances, it is more uniform and the image excellent in the concentration and saturation of an image is formed.

[0042] moreover — the time (drawing 7 (1)) of the liquid constituent 706 being given to recorded media 703, and the time of ink 713 being given to ***** 707 — (— when the dispersion medium which is distributing drawing 7 (2)) and a particle 709 changes, before distribution of a particle 709 becomes unstable and color material 704 adsorbs, what causes condensation between particles 709 exists. When change of a dispersion medium here points out physical-properties change of change generally observed, for example, pH of the liquid phase and solid content concentration, a solvent presentation, dissolved ion concentration, etc. when the liquid of a different kind beyond two sorts or it is mixed, and a liquid constituent contacts recorded media and ink, these change arises rapidly and complexly, destroys the distributed stability of a particle, and is considered to generate an aggregate.

[0043] It is surmised that these aggregates contribute to the further color-enhancing improvement by incorporating color material to the pore formed in the interior of the aggregate mentioned later. Moreover, although the aggregate formed within these ***** 707 has some which are sticking to recorded media, and what can move the inside of the liquid phase (it has a fluidity) exists, like the reaction process of the above-mentioned color material and a particle, color material stuck to the particle aggregate front face in the state of the single molecule, and formed the bigger aggregate on it, and this has also contributed what has a fluidity to color-enhancing improvement.

[0044] Moreover, in case the particle aggregate 711 which exists near the front face of the above-mentioned recorded media by using the liquid constituent of this invention is formed, the pore of a certain amount of magnitude is formed in the interior of an aggregate. The color material 704 which was not able to stick to the particle 709 in ***** 707 has some which permeate the interior of the particle aggregate 711 through pore with a solvent component. In that case, by sticking to near an inlet port and the pore wall of pore in a particle aggregate, more color material is efficient a front face and inside the particle aggregate 711, and color material 605 is adsorbed. Furthermore, since the pore diameter of the particle aggregate 711 is 1 to about several times the molecule size which exists in the ink of color material 704 when color

material 704 is a color, condensation of color material cannot take place very easily, and the color material 704 which stuck to the interior of pore becomes possible [forming an ideal single molecule condition]. This can contribute to the further color-enhancing improvement greatly, and can obtain the record object which has the still larger color reproduction range.

[0045] Moreover, the pore physical properties of the particle aggregate 711 found out not only the particle contained in a liquid constituent but image formation being [in which it turns out that it is influenced with a solvent presentation etc., a particle aggregate is formed in from a liquid constituent, and the pore volume in a specific pore-radius field with this particle aggregate is formed on recorded media] ability, and that functionality was very high.

[0046] Furthermore, with the energy 716 from the outside, while carrying out a polymerization within [whole] the coloring section 700, it converts into the polymer which carried out three-dimensions bridge formation, and solidifies, and a monomer 705 sticks a monomer 705 to recorded media (drawing 7 (4)). In that case, in order to remove a solvent component beforehand, it can consider as the firm thing which hardened the coloring section 700 effectively by giving a desiccation process. According to this hardening process, recorded media 703 are pasted firmly and improvement in scratch-proof nature or weatherability of the coloring section 700 is attained.

[0047] In addition, although these have so far been explained by the case where it gives recorded media, in order of a liquid constituent and ink, if the liquid-liquid reaction of ink and a liquid constituent is attained, the order of grant to the recorded media of ink and a liquid constituent is not restricted to this at all, and it is ink first. Subsequently, you may be the order which gives a liquid constituent.

[0048] The liquid constituent and ink by which this invention is characterized below are explained to a detail. First, the definition of the cationic ink in this invention or anionic ink is described. Lessons is taken from the ion property of ink, and the electric charge of unacquainted ink itself is not carried out, but it being neutrality is setting to the technical field concerned and known in itself. The component in ink, for example, color material, has an anionic radical or a cationic radical, and anionic ink here or cationic ink points out the ink currently adjusted so that these radicals may carry out behavior as an anionic radical or a cationic radical into ink. Moreover, the semantics is the same as that of the above also about an anionic or cationic liquid constituent.

[0049] The liquid constituent of this invention is explained below to a <liquid constituent>.

(Operation of a particle) When it mixes with adsorbing color material, without spoiling the color enhancement which color material originally has when it mixes with 1 ink, and 2 ink as an operation which the particle contained in a liquid constituent is expected in this invention, or when it is given to recorded media, distributed stability falling and remaining on the surface of recorded media etc. is mentioned. These operations may be attained by one sort or two sorts or more of particles.

[0050] It is mentioned that a particle presents ionicity contrary to color material as a property for fulfilling an operation of 1). Thereby, a particle can adsorb color material electrostatic. When color material is anionic, when color material is cationicity conversely, an anionic particle is used using a cationic particle. As an element which adsorbs color material in addition to ionicity, the configuration of the size, the mass, or the front face of a particle is mentioned. For example, the porosity particle which has much pores in a front face shows a characteristic adsorption property, and can adsorb color material in magnitude, a configuration, etc. of pore with two or more elements.

[0051] An operation of 2) is caused by the interaction with ink or recorded media. For this reason, although what is necessary is to just be attained by each configuration, presenting ionicity contrary to an ink presentation component or the constituent of recorded media as a property of a particle for example, is mentioned. Moreover, the distributed stability of a particle is influenced also by making an electrolyte live together in ink or a liquid constituent. In this invention, it is desirable to acquire one operation of the above 1 and the operations of two in an instant. Furthermore, it is desirable that an operation of the above 1 and 2 and both is acquired in an instant.

[0052] (Particle aggregate) Although a particle aggregate is formed near the front face of

recorded media of the specific particle contained when the liquid constituent of this invention is used for image formation although the mechanism of record described previously, the pore of a certain amount of magnitude is formed in the interior of this aggregate. Then, the color material which existed independently in ink Since the interior of pore of this particle aggregate is permeated and near an inlet port and the wall of pore are adsorbed in the state of an ideal single molecule in case ink permeates the interior of recorded media, color material It will remain near the front face of recorded media more mostly, and it becomes possible to obtain the record object which has the color enhancement which was further excellent with this.

[0053] Therefore, as for the liquid constituent of this invention, it is desirable to constitute so that moderate pore may be formed in a particle aggregate in the case of image formation. Here, the pore formed of the particle contained in a liquid constituent can be measured by the following approach. That is, by the following approach, by measuring the pore volume in a certain specific pore-radius field, and constituting so that this value may become suitable within the limits, the mechanism of the above-mentioned record is performed and good image formation becomes possible about the particle aggregate obtained from the liquid constituent which contains a particle and a solvent at least. In measuring the physical properties of these particle aggregates, the liquid constituent which is the measuring object is first pretreated in the following procedures.

[0054] (1) Dry the liquid constituent which the particle contains at 120 degrees C under an atmospheric-air ambient atmosphere for 10 hours, make the amount of solvent evaporate mostly, and dry.

(2) Calcinate at 700 degrees C for 3 hours after carrying out the temperature up of the above-mentioned dry matter from 120 degrees C to 700 degrees C in 1 hour.

(3) Return the above-mentioned baking object to ordinary temperature gradually after baking, and fine-particles-ize a baking object.

The reason for performing the above-mentioned pretreatment here is for making a particle aggregate form from a liquid constituent by desiccation, removing the solvent component in a liquid constituent completely, emptying pore inside an aggregate, and forming an opening by baking.

[0055] In this invention, the nitrogen adsorption ****ing method can be suitably used as the pore radius of the pore of a particle aggregate, and a measuring method of pore volume. In this invention, when the size of the pore of the particle aggregate measured by such approach had the pore volume in the field whose pore radius is 3nm - 30nm in the specific range, it turned out that good image formation becomes possible. Although the reason nil why functionality is high is not clear, when the pore volume in the size field of this pore considers as range which described the pore radius above to guess to image formation ability Since it is easy to produce the color material inside a particle aggregate, and osmosis of a solvent component, it is thought that adsorption of the color material resulting from pore increases, and by suppressing light scattering of the pore itself that it is for the amount of color material which participates in substantial color-enhancing improvement to increase.

[0056] Therefore, it is effective as a measuring method of the color-enhancing ability of the formation image which measuring the pore volume in the field whose pore radius is 3nm - 30nm, and the field exceeding 30nm formed using the liquid constituent about the particle aggregate formed when the above pretreatments are performed to the liquid constituent of the measuring object. As a measuring method of the pore physical properties in this field, the approach by the nitrogen adsorption ****ing method is the most desirable. After a pore radius and pore volume carry out the vacuum deairing of the pretreated above-mentioned liquid constituent sample at 120 degrees C for 8 hours, it can ask for them from the nitrogen adsorption ****ing method from Barrett's and others approach (J. Am.Chem.Soc., Vol 73, 373, and 1951). Furthermore, a desirable measuring method is measuring the pore volume in the field whose pore radius's is 3nm - 20nm, and the field exceeding 20nm about the pore formed in the particle aggregate. In this range, since much more color-enhancing improvement is especially obtained when color material is a color, when measuring this color-enhancing ability, it is desirable.

[0057] (The pore radius and pore volume of a particle aggregate) The pore radius of a particle

aggregate is considered that it is desirable that it is the range of 3nm – 30nm like the above-mentioned from a viewpoint which prevents the adsorption to prompt osmosis, near a pore inlet port, and the wall of color material, and condensation of the color material inside pore. Moreover, in order to incorporate only the color material which contributes to color-enhancing improvement inside, a certain amount of capacity is required for coincidence. Moreover, it is thought that the number of the pores in a particle aggregate also increases because pore volume increases, and it is thought that not only the amount of adsorption of the color material inside pore but the amount of adsorption near the inlet port of pore increases.

[0058] Therefore, the pore volume in the range whose pore radius is 3nm – 30nm is 0.4 or more ml/g, and the liquid constituent used suitable for this invention from these viewpoints has that desirable whose pore volume in the field in which a pore radius exceeds 30nm is 0.1ml/g or less, when the pore in a particle aggregate is measured by approach which was described above. In pore with a pore radius smaller than 3nm, neither color material nor a solvent component can permeate the interior of pore easily, and the pore of a particle aggregate does not contribute to color-enhancing improvement substantially. Moreover, since there is much pore with big light scattering when pore volume exceeds 0.1 ml/g in the field to which a pore radius exceeds 30nm, it is hard coming to contribute the color material which stuck near a pore inlet port and to a wall to color enhancement. Moreover, since there are few the color material and the solvent components which permeate the interior of a particle aggregate when the pore volume in the field of the above-mentioned pore radius is under this range, the amount of color material which sticks to near an inlet port and the interior of pore decreases and the contribution to color-enhancing improvement becomes low, it is not desirable.

[0059] As more desirable range, the pore volume in the range whose pore radius is 3nm – 20nm is 0.4 or more ml/g, and it is desirable to use that whose pore volume in the field in which a pore radius exceeds 20nm is 0.1 or less ml/g. When the pore of the range of a radius whose pore is 3nm – 20nm exists mostly, and a color is especially used for color material, color enhancement improves further and can form the image which has the still larger color reproduction range. The pore radius and pore volume of the particle aggregate formed from a liquid constituent change with the chemical species of the particle contained, a configuration and not only magnitude but a solvent kind, other additives, those presentation ratios, etc., and are considered that the formation condition of a particle aggregate is controllable by controlling these conditions. Therefore, when producing the liquid constituent of this invention, it is desirable to take these things into consideration and to make it the configuration of the pore formed in a particle aggregate become within the limits of the above.

[0060] Next, the liquid constituent containing cationicity or an anionic particle is explained concretely.

[Cationic liquid constituent] As a cationic liquid constituent, the liquid constituent with which stability comes to distribute this particle is mentioned, for example including the particle which has a cationic radical on a front face. In this invention, the thing by which pH was adjusted to 2–7 as a cationic liquid constituent including the acid, and the thing whose F-potential is +5–+90mV can be used suitably.

[0061] (pH and F-potential) The F-potential of a liquid constituent is described. The basic principle of F-potential is shown below. Generally, when an isolation charge is on the surface of solid phase in the system which the solid-state is distributing in a liquid, it appears so that the electric charge layer of an opposite charge may maintain electrical neutrality at the liquid phase near a solid phase interface. This is called an electric dipole layer and is calling F-potential the thing of the potential difference by this electric dipole layer. When F-potential is plus, the front face of a particle shows cationicity and shows anionic by minus. Generally, the electrostatic repulsive force committed between particles becomes strong, dispersibility is said to be good, and it is possible that the ionicity on the front face of a particle is strong to coincidence, so that the absolute value is high. That is, it can be said that cationicity is so strong that the F-potential of a cationic particle is high, and the force which draws the anionic compound in ink is strong.

[0062] When the liquid constituent which is in the range whose F-potential is +5–+90mV as a result of this invention persons' inquiring wholeheartedly was used, the coloring section which it

comes to form on recorded media found out presenting the especially excellent coloring property. Although the reason is not certain, since the cationicity of a particle is moderate and an anionic compound probably sticks to homogeneity thinly on a particle front face, without condensation of a rapid anionic compound (anionic color material) taking place, it is thought that it is hard to form a lake with a huge color material, consequently the coloring property of color-material original is discovered in the better condition. Furthermore, with the cationic liquid constituent of this invention, even after adsorbing an anionic compound on a particle front face, while a particle condenses a particle presenting weak cationicity because it will be in a distributed unstable state, it adsorbs easily on the surface of recorded media, and it is thought that it is easy to remain near the front face of recorded media.

[0063] Consequently, it is thought that the next outstanding effectiveness is acquired. That is, in an image field with many the coloring property which was excellent in the coat paper average for ink jets also to media, such as not only a regular paper but an absorbency scarce plastics metallurgy group, and the amounts of ink grants, such as the shadow section and the solid section, there are little white MOYA and color nonuniformity and they become the thing excellent in the homogeneity of a color. Moreover, since the amount of grants of a cationic particle can also be lessened in order that an anionic compound may adsorb and color to a particle very efficiently compared with coat paper, when it especially prints in a regular paper, aesthetic property of paper is not spoiled and it excels also in the scratch-proof nature of a record image. When F-potential uses the liquid constituent containing the cationic particle in the range which is +10→85mV as range of more desirable F-potential, for example When solid printing is carried out, the boundary between dots stops being able to be conspicuous easily, and much more reduction of stripe nonuniformity with a head scan can be attained. Further If F-potential uses the liquid constituent containing a cationic particle in the range which is +15→+65mV, it will not be based on a medium kind but it will become possible to obtain the image which has the extremely excellent color enhancement.

[0064] As for pH of the cationic liquid constituent of this invention, it is desirable that it is in the range of 2-7 near 25 degree C from an adsorbent viewpoint of preservation stability and an anionic compound. Since the stability of an anionic compound is not remarkably reduced when a liquid constituent is mixed with anionic ink within the limits of this pH, strong condensation of anionic compounds is not caused, and the saturation of a record image can fall or it can prevent becoming the somber image effectively. Moreover, since the distributed condition of a cationic particle is also good in above-mentioned it being within the limits, the preservation stability of a liquid constituent and the regurgitation stability from a recording head are maintainable good. Furthermore, when it mixes with ink, since a cationic particle front face is fully adsorbed, the anionic matter can obtain the outstanding color-enhancing ink jet record object. As range of more desirable pH, pH is 3-6, and in this range, while being able to prevent the corrosion of the recording head by the mothball very effectively, it improves one layer of scratch-proof nature nearby of a record image.

[0065] (Cationic particle) Next, the component which constitutes the cationic liquid constituent of this invention is described. The cationic particle mentioned as the 1st component requires that the front face of the particle itself presents cationicity in the condition of having distributed in the liquid constituent, in order to attain the above-mentioned operation effectiveness. When it mixes with anionic ink by making a front face into cationicity, an anionic color material sticks to a particle front face promptly, and the ink jet record object of sufficient image concentration is obtained by leaving color material to homogeneity on a recorded-media front face in the state of a single molecule. On the other hand, a particle front face is not cationicity, and when the particle and the water-soluble cationic compound exist separately in a liquid constituent, in order that color material may spoil the coloring property of a lifting and the color material itself for condensation centering on a cationic compound, it becomes difficult to attain the color enhancement of the coat paper average for ink jets. Therefore, although the front face needs to be cationicity, if the particle used for the liquid constituent of this invention is a particle by which the front face was cation-ized by processing even if it is a particle which is originally anionic or neutrality electrostatic not to mention the particle which is essentially cationicity, it

can be used for the liquid constituent of this invention.

[0066] If pore is formed in the aggregate by these particles formed on recorded media, the cationic particle suitably used by this invention will come out enough for attaining the purpose of this invention, and, for a certain reason, will not be especially limited to the ingredient kind of a particle. As an example, the silica and alumina which were cation-ized, hydrated alumina, a titania, a zirconia, boria, silica boria, Seria, a magnesia, a silica magnesia, a calcium carbonate, a magnesium carbonate, a zinc oxide, hydrotalcites, etc. these compound particles, an organic particle, an inorganic organic compound particle, etc. are mentioned, for example. These cationic particles can mix and use one sort or two sorts or more.

[0067] Since the particle front face has positive charge when hydrated alumina is used especially as a particle, it is desirable, and it is desirable in respect of the color enhancement excellent in the hydrated alumina which is an X-ray diffraction method and shows α -dynamite structure especially, the homogeneity of a color, preservation stability, etc. Hydrated alumina is defined by the following general formula.

aluminum $2O$ — the inside of $3-n(OH) 2n$ and, and the mH_2O above-mentioned type, and n — one of the integers of 0-3 — expressing — m — 0-10 — it has the value of 0-5 preferably. In many cases, the expression of mH_2O cannot express the aqueous phase which does not participate in formation of a crystal lattice and which can be α -dynamited, and the value whose m is not an integer can also be taken. However, in m and n , 0 does not become coincidence.

[0068] The (020) field is the stratified compound which forms a huge flat surface, and the crystal of hydrated alumina in which boehmite structure is generally shown shows a diffraction peak peculiar to an X-ray diffraction pattern. The structure which is called the pseudo-boehmite other than perfect boehmite and which contained superfluous water between the layers of a field (020) can also be taken. The X-ray diffraction pattern of this pseudo-boehmite shows a diffraction peak [broadcloth / boehmite].

[0069] Since distinction of boehmite and pseudo-boehmite is clearly impossible, unless it refuses, especially by this invention, it is called the hydrated alumina (henceforth hydrated alumina) which shows boehmite structures including both. (020) a field — a spacing — crystal thickness measures the peak to which diffraction rate 2θ appears in 14-15 degrees, whenever [angle-of-diffraction / of a peak], from 2θ and half-value width B , a spacing is Bragg's (Bragg) formula and and (020) can ask for crystal thickness using the formula of SHIERA (Scherrer). (020) The spacing of a field can be used as the hydrophilic property and the hydrophobic standard of hydrated alumina. Although not limited, if it is the approach that hydrated alumina with boehmite structure can be manufactured, especially as the manufacture approach of hydrated alumina used by this invention, it can manufacture by well-known approaches, such as hydrolysis of an aluminum alkoxide, and hydrolysis of a sodium aluminate, for example.

[0070] The hydrated alumina of amorphism can be changed and used for boehmite structure by heat-treating above 50 degrees C under existence of water in X diffraction as indicated by JP,56-120508,A. Especially the approach of using preferably is an approach of obtaining hydrated alumina, by adding an acid to a long-chain aluminum alkoxide, and performing hydrolysis and amalgam decomposition. Here, carbon numbers are five or more alkoxides, and when the alkoxide of carbon numbers 12-22 is used further, since removal of the alcohol content in a manufacture process and configuration control of hydrated alumina become easy so that it may mention later, it is desirable [a long-chain aluminum alkoxide].

[0071] as the acid to add — one sort out of an organic acid and an inorganic acid — or although two or more sorts can be chosen freely and can be used, a nitric acid is the most desirable in respect of the reaction effectiveness of hydrolysis and the obtained configuration control of hydrated alumina, or dispersibility. It is also possible to perform hydrothermal synthesis etc. after this process and to control particle diameter. If hydrothermal synthesis is performed using the dispersion liquid of the hydrated alumina containing a nitric acid, the nitric acid in a water solution is incorporated as a nitric-acid root on a hydrated alumina front face, and it can raise water-dispersion [of this hydrate]. Moreover, after hydrothermal synthesis, an acid can be suitably added to a hydrated alumina slurry, and the hydrated alumina slurry of very stable high

solid content concentration can be prepared by little acid concentration by adjusting and condensing pH. When such a slurry is used, the liquid constituent which did not need to ** separately the acid mentioned later outside and was excellent in the distributed stability of a hydrated alumina particle can be produced.

[0072] The approach by hydrolysis of the above-mentioned aluminum alkoxide has the advantage of being hard to mix impurities, such as various ion, as compared with the approach of manufacturing an alumina hydrogel and a cationic alumina. Furthermore, as for a long-chain aluminum alkoxide, the long-chain alcohol after hydrolysis also has the advantage that dealcoholization of hydrated alumina can be performed completely, as compared with the case where the alkoxide of short chains, such as aluminiumisopropoxide, is used. As for pH of the solution at the time of initiation of hydrolysis, setting less than to six is desirable. Since the hydrated alumina finally obtained will become a crystalline substance if pH exceeds 8, it is not desirable.

[0073] Moreover, as hydrated alumina used by this invention, if boehmite structure is shown with an X-ray diffraction method, the hydrated alumina containing metallic oxides, such as a titanium dioxide, can also be used. Since optical density becomes high, 0.01 – 1.00 mass % of hydrated alumina is desirable, and it is 0.13 to 1.00 mass % more preferably, the rate of adsorption of color material becomes quick, and a blot and beading stop easily being able to generate the content ratio of metallic oxides, such as a titanium dioxide. Furthermore, said titanium dioxide requires that the valence of titanium should be + tetravalence. The content of a titanium dioxide can be dissolved to boric acid, and can be investigated by the ICP method. Moreover, distribution of the titanium dioxide in hydrated alumina and the valence of titanium can be analyzed using ESCA.

[0074] It can reach for 100 seconds with argon ion, the front face of hydrated alumina can be etched for 500 seconds, and change of the content of titanium can be investigated. If the valence of titanium becomes smaller than + tetravalence, a titanium dioxide will come to commit a titanium dioxide as a catalyst, the weatherability of a record image falls or yellowing of a record image becomes easy to take place.

[0075] content of a titanium dioxide — the near front face of hydrated alumina — although it is good, you may contain to the interior. Moreover, a content may be missing from the interior and may be changing from the front face. If the titanium dioxide contains only very near the front face, since the electrical characteristics of hydrated alumina will be easy to be maintained, it is still more desirable.

[0076] as the manufacture approach of the hydrated alumina containing a titanium dioxide — ***** "surface science" — the method of hydrolyzing and manufacturing the mixed liquor of an aluminum alkoxide which is indicated by the 327th page (the volume for Kenji Tamaru, 1985), and a titanium alkoxide is desirable. When hydrolyzing the mixed liquor of said aluminum alkoxide and titanium alkoxide as the other approaches, hydrated alumina can also be added and manufactured as a nucleus of crystal growth.

[0077] Instead of a titanium dioxide, oxides, such as a silica, magnesium, calcium, strontium, barium, zinc, boron, germanium, tin, lead, a zirconium, an indium, phosphorus, vanadium, niobium, a tantalum, chromium, molybdenum, a tungsten, manganese, iron, cobalt, nickel, and a ruthenium, are made to contain, and can be used. For example, the hydrated alumina containing a silica has effectiveness in improvement in the scratch-proof nature of a record image.

[0078] The liquid constituent which the hydrated alumina used suitable for this invention was the thing of the range whose spacing of that (020) field is 0.614–0.626nm, and whose distributed stability of the hydrated alumina particle in the inside of a liquid constituent was good within the limits of this, and was excellent in preservation stability or regurgitation stability is obtained. Although this reason is not certain, if [above-mentioned] the spacing of a field (020) is within the limits, since it is the range where both the ratios of the hydrophobicity of hydrated alumina and a hydrophilic property are moderate, that to which the regurgitation stability of a liquid constituent becomes good is conjectured in a liquid constituent according to distributed being stability by moderate repulsion of particles, or the wettability balance inside a delivery being moderate.

[0079] Moreover, the range of hydrated alumina whose crystal thickness of that (020) field is

4.0–10.0nm is desirable, and since transparency and adsorbent [of color material] are excellent in it being this within the limits, it is desirable. Since correlation has the crystal thickness of the spacing of a field (020), and a field (020) according to this invention persons' knowledge, if the spacing of a field (020) is above-mentioned within the limits (020), the crystal thickness of a field can be adjusted to the range of 4.0–10.0nm.

[0080] Furthermore, since the alumina (aluminum oxide) generated by heat treatment of calcining (calcination) etc. in the above-mentioned hydrated alumina, metal aluminum, or an aluminum salt has positive charge similarly, it is used suitably. As an alumina, there are alpha mold, gamma mold, and a thing that has the crystallized state of delta, chi, eta, rho, beta mold, etc. further, it is the form where the front face was maintained at cationicity, and all can be used if it distributes stably underwater. Especially, a front face is activity, gamma mold has the high adsorption power of color material, since it also tends to form the stable particle dispersing element atomized comparatively, is excellent in color enhancement, shelf life, regurgitation stability, etc., and can be used suitably.

[0081] Moreover, as for a cationic particle which is used by this invention and which was described above, the thing of the range whose mean particle diameter measured by the dynamic-light-scattering method is 0.005–1 micrometer is suitably used from viewpoints, such as color enhancement after printing, the homogeneity of a color, and preservation stability. Within the limits of this, too much osmosis can be effectively prevented inside absorbency high recorded media like a regular paper, and the homogeneous fall of color enhancement or a color can be suppressed. Moreover, it is also suppressed that a cationic particle sediments in a liquid constituent, and it can also prevent the fall of the preservation stability of a liquid constituent effectively. More preferably, mean particle diameter is a thing within the limits which are 0.01–0.8 micrometers, and if such a particle is used, the texture of the scratch-proof nature of the image after printing to recorded media, or a record object will become desirable especially. Furthermore, mean particle diameter is a thing within the limits which are 0.03–0.3 micrometers, and since the pore of the particle aggregate formed on recorded media is easy to be formed effectively in the pore-radius field made into the purpose, such a particle has it. [preferably desirable]

[0082] (The pore physical properties and configuration of a cationic particle) It makes color material stick to the front face of the particle itself efficiently, and also the maximum pore radius of the particle in the nitrogen adsorption ****ing method is 2–12nm, and that whose total pore volume is 0.3 or more ml/g is desirable [a particle] again at the same time a cationic particle which is used by this invention and which was described above forms efficiently the pore of the particle aggregate formed on recorded media. The maximum pore radius of a particle is 3m – 10nm more preferably, and since the pore of the particle aggregate formed on recorded media is easy to be formed effectively in the pore-radius field made into the purpose, that whose total pore volume is 0.3 or more ml/g is desirable.

[0083] When the adsorption site of the color material on the front face of a particle exists enough that it is within the limits the BET specific surface area of whose is 70–300m²/g, the above-mentioned particle used by this invention becomes easy to leave color material near the front face of recorded media in the state of a single molecule more effectively, and contributes to color-enhancing improvement.

[0084] Moreover, the configuration of the particle used by this invention can make ion exchange water able to distribute a particle, can be dropped on a collodion membrane, can produce a test sample, and can observe and ask for it with a transmission electron microscope. In case a particle aggregate is made to form on recorded media in this invention, it is the point of making pore forming in an aggregate, and the non-globular form thing in which the particle configuration forms the aggregated particle which the shape of a needle, the monotonous configuration, or the spherical primary particle had a certain directivity, and was connected, such as the shape of the shape of a rod or a necklace, can be used suitably.

[0085] According to this invention persons' knowledge, plate-like one of the dispersibility to water is better than the shape of a needle, and a pilliform bundle (cilia **), and since the orientation of a particle becomes random when a particle aggregate is formed and pore volume

becomes large, the configuration of a particle is more desirable. A pilliform bundle configuration means the condition that the needlelike particle touched in side faces and gathered like the bundle of the hair of hair here. it is indicated by reference (Rocek J., etal, Applied Catalysis, 74 volumes, 29-36 pages, 1991) at pseudo-boehmite also in the hydrated alumina which can be preferably used especially by this invention — as — cilia — generally it is known that there are a ** and the other configuration.

[0086] It can ask for the aspect ratio of the particle of a monotonous configuration by the approach defined as JP,5-16015,B. An aspect ratio is shown by the ratio of a diameter to the thickness of a particle. The diameter of circle which has an area equal to the projected area of the particle when observing hydrated alumina with a microscope or an electron microscope shall be indicated to be a diameter here. An aspect ratio is expressed in the ratio of the diameter which observes similarly and shows the minimum value of a monotonous side, and the diameter which shows maximum as an aspect ratio. Moreover, in the case of a pilliform bundle configuration, the method of asking for an aspect ratio can find an up-and-down diameter of circle and die length, respectively by the ability using as a cylinder each needlelike hydrated alumina particle which forms a pilliform bundle, and can take and ask it for the ratio. the configuration of the most desirable hydrated alumina — plate-like — an average aspect ratio — the range of 3-10 — moreover, by the pilliform bundle, the range of 3-10 has a desirable average aspect ratio. Since a clearance is easy to be formed between particles when the average aspect ratio was within the limits and it forms [above-mentioned] a particle aggregate, a vesicular structure can be formed easily.

[0087] The content of a cationic particle in the liquid constituent of this invention which was described above is the range suitable although what is necessary is just to determine the optimal range suitably, when the range of 0.1 – 40 mass % attains the purpose of this invention according to the class of matter to be used, and the range of one to 30 mass %, and further 3 – 15 mass % is more preferably suitable for it. At such within the limits, the image of coloring which depended and was excellent in the medium kind can be obtained to stability, and it excels also especially in the preservation stability and regurgitation stability of a liquid constituent.

[0088] (Acid) As stated previously, as for the liquid constituent of this invention, it is desirable that pH is adjusted to 2-7 including an acid. While an acid raises the distributed stability of the particle in the inside of liquid by ionizing a cationic particle front face and raising surface potential, the role of the adsorption disposition top of the anionic compound in ink (anionic color material) and the viscosity control of a liquid constituent is played. Combining the cationic particle to be used, the acid used suitable for this invention will not be limited, especially if physical properties, such as desired pH, and F-potential or particle dispersibility, are acquired, but it can be used, choosing it to the next inorganic acid, the next organic acid, etc. freely.

[0089] As an inorganic acid, a hydrochloric acid, a sulfuric acid, a sulfurous acid, a nitric acid, a nitrous acid, phosphoric acid, boric acid, carbonic acid, etc. are mentioned, and, specifically, a carboxylic acid which is listed below, a sulfonic acid, amino acid, etc. are mentioned as an organic acid, for example.

[0090] As a carboxylic acid, for example A formic acid, an acetic acid, a chloroacetic acid, dichloroacetic acid, A trichloroacetic acid, gifblaar poison, trimethylacetic acid, a methoxy acetic acid, mercaptoacetic acid, A glycolic acid, a propionic acid, butanoic acid, a valeric acid, a caproic acid, a caprylic acid, A capric acid, a lauric acid, a myristic acid, a palmitic acid, stearin acid, Oleic acid, linolic acid, a linolenic acid, cyclohexane carboxylic acid, A phenylacetic acid, a benzoic acid, ortho toluylic acid, meta toluylic acid, para toluylic acid, O-chlorobenzoic acid, m-chloro benzoic acid, para chlorobenzoic acid, o-BUROMO benzoic acid, m-BUROMO benzoic acid, p-BUROMO benzoic acid, o-nitro benzoic acid, m-nitro benzoic acid, P-nitrobenzoic acid, oxalic acid, a malonic acid, a succinic acid, a glutaric acid, An adipic acid, a tartaric acid, a maleic acid, a fumaric acid, a citric acid, a phthalic acid, Isophthalic acid, a terephthalic acid, a salicylic acid, para hydroxybenzoic acid, an anthranilic acid, m-aminobenzoic acid, p-aminobenzoic acid, o-methoxy benzoic acid, m-methoxy benzoic acid, para methoxy benzoic acid, etc. are mentioned.

[0091] Moreover, as a sulfonic acid, benzenesulfonic acid, a methylbenzene sulfonic acid, an

ethylbenzene sulfonic acid, dodecylbenzenesulfonic acid, 2 and 4, 6-trimethyl benzenesulfonic acid, 2, 4-dimethylbenzene sulfonic acid, 5-sulfosalicylic acid, 1-sulfo naphthalene, 2-sulfo naphthalene, a hexane sulfonic acid, an octane sulfonic acid, a dodecane sulfonic acid, etc. are mentioned, for example.

[0092] Moreover, as amino acid, a glycine, an alanine, a valine, alpha-aminobutyric acid, gamma-aminobutyric acid, the beta-alanine, a taurine, a serine, epsilon-amino-n-caproic acid, a leucine, a norleucine, a phenylalanine, etc. are mentioned.

[0093] and the liquid constituent of this invention — setting — these acids — one sort — or two or more sorts can use it, mixing. Also in these acids, since it excels in the distributed stability of a cationic particle, or adsorbent [of an anionic compound], the underwater primary dissociation constant pK_a can use especially five or less thing suitably. Specifically as such an acid, a hydrochloric acid, a nitric acid, a sulfuric acid, phosphoric acid, an acetic acid, a formic acid, oxalic acid, a lactic acid, a citric acid, a maleic acid, a malonic acid, etc. are mentioned.

[0094] It is desirable when making it A:B=200:1-5:1 and become the range of 150:1-8:1 more preferably aims at improvement in the distributed stability of a cationic particle, and adsorbent improvement to the particle front face of an anionic compound for the mixed ratio of a cationic particle (A) and an acid (B) in a liquid constituent on mass criteria in the liquid constituent of this invention.

[0095] (Other constituents) Next, the component of others which constitute a cationic liquid constituent is explained concretely. Although the cationic liquid constituent of this invention usually contains water as a solvent object, including the above-mentioned cationic particle, an acid, a photopolymerization initiator which was preferably described above, etc., its thing containing the organic solvent for dissolving the further below-mentioned monomer and other additives is desirable.

[0096] As an organic solvent to be used, for example In this case, dimethylformamide, amides [, such as dimethylacetamide,]: — ketones [, such as an acetone,]: — a tetrahydrofuran — Polyalkylene glycols, such as ether, such as dioxane, a polyethylene glycol, and a polypropylene glycol : Ethylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, Alkylene glycol, such as a diethylene glycol : Ethylene glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol monomethyl ether and the triethylene glycol monomethyl ether : Ethanol, [others / monohydric alcohol, such as isopropyl alcohol, n-butyl alcohol, and isobutyl alcohol,] A glycerol, a N-methyl-2-pyrrolidone, 1, 3-dimethyl-imidazolidinone, Aliphatic hydrocarbon, such as aromatic-hydrocarbon:hexanes, such as benzene, such as triethanolamine, a sulfolane, and dimethyl sulfoxide, toluene, and a xylene, an octane, and a heptane, Propylene carbonate etc. is mentioned. Although there is especially no limit about the content of the above-mentioned organic solvent, further 5 - 60% is the suitable range 5 to 90% of liquid constituent all mass, for example.

[0097] Moreover, additives, such as a viscosity controlling agent, pH regulator, antiseptics, various surface active agents, an anti-oxidant and an evaporation accelerator, a water-soluble cationic compound, and binder resin, may be further blended with the liquid constituent of this invention suitably if needed. Especially selection of a surfactant is important, when [to the recorded media of a liquid constituent] getting wet and adjusting *****. For the purpose of control of the bleeding in unique image fields, such as the further cationic grant of a liquid constituent, improvement in alphabetic character grace, etc., in the range which does not check the operation effectiveness of this invention, a water-soluble cationic compound is chosen freely and can be added.

[0098] As a water-soluble cationic compound, specifically For example, the poly allylamine, a polyamine sulfone, a polyvinyl amine, The neutralization object or partial neutralization objects by the acid, such as chitosan and these hydrochloric acids, or an acetic acid, The compound which cation-ized some Nonion nature compounds of a giant molecule For example, the copolymer of vinyl pyrrolidone and the 4th class salt of an amino alkyl alkylate, It can be used from a copolymer, etc. a compound of the 1st class, the 2nd class, and a tertiary amine salt type, such as a cationic surfactant, in addition to this, an amino acid mold amphoteric compound, etc. of acrylamide and the 4th class salt of aminomethyl acrylamide, being able to choose one sort or

two sorts or more.

[0099] Binder resin is the purposes, such as improvement in the further scratch-proof nature of a cationic particle, it can be used together in the range which does not spoil the preservation stability or regurgitation stability of the texture of recorded media, or a liquid constituent, for example, can be freely chosen to a water-soluble polymer, a polymer emulsion, polymeric latex, etc., and can be used. Moreover, as mentioned later, it is a desirable gestalt in the preservation stability of a liquid constituent and ink to add a photopolymerization initiator and a sensitizer in a liquid constituent at the same time it promotes efficiently hardening (a monomer should carry out a polymerization and a generation polymer object should construct a bridge by grant of energy) of a monomer.

[0100] (Surface tension of a liquid constituent) The liquid constituent of this invention may be toned according to the color of recorded media, although colorlessness or a white thing is more desirable. Furthermore, as suitable range of the various physical properties of the above liquid constituents, surface tension is more preferably made into 10 – 40 mN/m (dyn/cm) ten to 60 mN/m (dyn/cm), and viscosity is made into 1 – 30 mPa·s (cP).

[0101] Although the anionic liquid constituent of [anionic liquid constituent] this invention makes an indispensable constituent the particle which has an anionic radical on a front face and is characterized by this particle distributing to stability, that by which pH is further adjusted to 7–12 including the base, and its thing whose F-potential is –5–90mV are desirable.

[0102] (pH and F-potential) As a result of this invention persons' inquiring wholeheartedly, it found out that the anionic liquid constituent in the range whose F-potential is –5–90mV presented the coloring property in which the front face of an anionic particle was especially adsorbed especially efficiently, and the cationic compound in ink (cationic color material) was excellent on recorded media. Although the reason is not certain, as well as the case of the cationic liquid constituent probably explained previously since anionic [of a particle] is moderate, color material does not form a huge lake in a particle front face by sticking to homogeneity thinly, without rapid condensation of the cationic compound in ink taking place, but it is thought that the coloring property of color-material original is discovered better.

Furthermore, in the anionic liquid constituent of this invention, after adsorbing a cationic compound on a particle front face, it becomes distributed instability, and it is thought that particles condense by the concentration change at the time of a solvent component evaporating and permeating on recorded media, and it becomes easy to remain near the front face.

[0103] Consequently, it is thought that the next outstanding effectiveness is acquired. That is, in an image field with many amounts of ink grants, such as the coloring property and the shadow section which were excellent in the coat paper average for ink jets, and the solid section, white MOYA and color nonuniformity are excellent in the homogeneity of a color few. Moreover, in order for a cationic compound to stick to a particle front face and to color on it very efficiently compared with coat paper, when the amount of grants of an anionic particle can also be lessened and is especially printed in a regular paper, the aesthetic property of paper is maintained, and the scratch-proof nature of a record image also becomes good. The range of the range of more desirable F-potential is –10–85mV, when the liquid constituent containing the anionic particle which has the F-potential of such range is used, and it carries out solid printing, the boundary between dots stops being able to be conspicuous easily, and it can attain much more reduction of stripe nonuniformity with a head scan. Furthermore, if F-potential uses preferably the liquid constituent containing the anionic particle in the range which is –15–65mV, it will not be based on a recorded-media kind, but it will become possible to obtain the image which has the extremely excellent color enhancement.

[0104] As for pH of the anionic liquid constituent of this invention, it is desirable that it is the range of 7–12 near [an adsorbent viewpoint to] 25 degree C of the cationic compound in preservation stability and ink. Since the stability of a cationic compound (color material) is not remarkably reduced when it mixes with cationic ink to this pH within the limits, strong condensation of cationic compounds is not caused, and the saturation of a record image can fall or it can prevent becoming the somber image effectively. Moreover, if there is pH within above limits, since the dispersibility of an anionic particle is also good, the preservation stability of a

liquid constituent and the regurgitation stability from a recording head are maintainable good. Furthermore, when it mixes with ink, the color-enhancing ink jet record object in which the anionic particle front face was fully adsorbed, and the cationic matter was excellent is obtained. The range of pH of a more desirable liquid constituent is 8-11, and it improves one layer of scratch-proof nature nearby of a record image while it can prevent the corrosion of the recording head by the mothball very effectively, if pH is this within the limits.

[0105] (Anionic particle) Next, the component which constitutes the anionic liquid constituent of this invention is described. In order to attain the above-mentioned operation effectiveness, as for the anionic particle mentioned as 1st indispensable component, it is desirable that it is what the front face of the particle itself presents anionic in the condition of having distributed in the liquid constituent. When it mixes with cationic ink by making a particle front face anionic, a cationic color material can be adsorbed on a particle front face, and the ink jet record object of sufficient image concentration is obtained by leaving color material to homogeneity on a recorded-media front face in the state of a single molecule.

[0106] On the other hand, a particle front face is not anionic, and when the particle and the water-soluble anionic compound exist separately in a liquid constituent, in order that color material may spoil the coloring property of a lifting and the color material itself for condensation centering on an anionic compound, it becomes difficult to attain the color enhancement of the coat paper average for ink jets. Therefore, although it is required to have charged the front face in anionic, the particle used with the liquid constituent of this invention can be used if it is the particle by which the front face was anion-ized by processing, even if it is originally a cationic or neutral particle electrostatic not to mention the particle which is essentially anionic.

[0107] The anionic particle suitably used by this invention is enough to attain the purpose of this invention if pore is formed in the aggregate by these particles formed on recorded media, and especially the ingredient kind of a particle is not limited. As an example, the silica and titania which were anion-ized, a zirconia, boria, silica boria, Seria, a magnesia, a silica magnesia, a calcium carbonate, a magnesium carbonate, zinc oxides, etc. these compound particles, an organic particle, an inorganic organic compound particle, etc. are mentioned, for example. and the liquid constituent of this invention — setting — these — one sort — or two or more sorts can use it, mixing.

[0108] Moreover, the thing of the range whose mean particle diameter measured by the dynamic-light-scattering method from a viewpoint of the color enhancement of the ink after printing, the homogeneity of a color, and preservation stability is 0.005-1 micrometer is suitable for the anionic particle used by this invention like the case of the cationic particle explained previously. More preferably, mean particle diameter is a thing within the limits which are 0.01-0.8 micrometers, and if such a particle is used, scratch-proof nature and texture after printing to recorded media will become desirable especially. Furthermore, mean particle diameter is a thing within the limits which are 0.03-0.3 micrometers, and since the pore of the particle aggregate formed on recorded media is easy to be formed effectively in the pore-radius field made into the purpose, such a particle has it. [preferably desirable]

[0109] (The pore physical properties and configuration of an anionic particle) An anionic particle which is used by this invention and which was described above has that desirable whose total pore volume the maximum pore radius of the particle by the nitrogen adsorption ****ing method is 2-12nm, and is 0.3 or more ml/g when making color material stick to the front face of the particle itself efficiently at the same time it forms efficiently the pore of the particle aggregate formed on recorded media again. The maximum pore radius of a particle is 3-10nm more preferably, and since the pore of the particle aggregate formed on recorded media is easy to be formed effectively in the pore-radius field made into the purpose, that whose total pore volume is 0.3 or more ml/g is desirable.

[0110] When the adsorption site of the color material on the front face of a particle exists enough that it is within the limits the BET specific surface area of whose is 70-300m²/g, the particle used by this invention becomes easy to leave color material near the front face of recorded media in the state of a single molecule more effectively, and contributes to color-enhancing improvement.

[0111] Moreover, the configuration of the particle used by this invention can make ion exchange water able to distribute a particle, can be dropped on a collodion membrane, can produce a test sample, and can observe and ask for it with a transmission electron microscope. In case a particle aggregate is made to form on recorded media in this invention, it is the point of making pore forming in an aggregate, and a non-globular form thing, such as the shape of the shape of a needle, a monotonous configuration or the shape of a rod which forms the aggregated particle connected with directivity with a spherical primary particle, or a necklace, can be suitably used for a particle. According to this invention persons' knowledge, since the dispersibility to water becomes [a needlelike twist / the orientation of a particle] random when the plate-like configuration is better and it forms a particle aggregate and pore volume becomes large, a particle is more desirable.

[0112] The content in the liquid constituent of an anionic particle which was described above is the range suitable when considering as the range of 0.1 – 40 mass % although what is necessary is just to determine the optimal range suitably attains the purpose of this invention according to the class of matter to be used, and the range of one to 30 mass %, and further 3 – 15 mass % is more preferably suitable for it. At such within the limits, it is not based on a medium kind, but the image of outstanding coloring can be obtained to stability, and it excels also especially in the preservation stability and regurgitation stability of a liquid constituent.

[0113] (Base) As stated previously, as for the anionic liquid constituent of this invention, it is desirable that pH is adjusted to 7–12 including a base. A base ionizes an anionic particle front face, and it plays the role of the viscosity control of the adsorption disposition top of the cationic compound in ink (cationic color material), or a liquid constituent while raising the distributed stability of the anionic particle in the inside of liquid by raising surface potential. When the base used suitable for this invention is combined with the anionic particle to be used, if physical properties, such as desired pH, F-potential, and particle dispersibility, are acquired, there is especially no limitation, and it can be used, choosing it to an inorganic compound, an organic compound, etc. which are listed below freely.

[0114] Specifically For example, a sodium hydroxide, a lithium hydroxide, a sodium carbonate, An ammonium carbonate, ammonia, sodium acetate, ammonium acetate, A morpholine, monoethanolamine, diethanolamine, triethanolamine, Ethyl monoethanolamine, n-butyl monoethanolamine, dimethylethanolamine, Alkanolamines, such as diethyl ethanolamine, ethyl diethanolamine, n-butyl diethanolamine, dinormal butyl ethanolamine, monoisopropanolamine, diisopropanolamine, and tri-isopropanolamine, can be used. Also in these, especially, since especially five or less base excels [dissociation constant / pkb / underwater / of a base / primary] in the distributed stability of an anionic particle, or adsorbent [of a cationic compound (cationic color material)], it is used suitably.

[0115] On mass criteria, it is the range of 150:1–8:1 more preferably, and A:B=200:1–5:1 and since it excels in the distributed stability of an anionic particle, and adsorbent [of the cationic compound on this front face of a particle], the mixed ratio of the anionic particle (A) in the inside of the liquid constituent of this invention and a base (B) is desirable.

[0116] (Other constituents) Next, the component of others which constitute an anionic liquid constituent is explained concretely. The anionic liquid constituent of this invention uses the above-mentioned anionic particle as an indispensable component. Although water is usually included as a solvent object, including a base which was preferably described above Furthermore, additives, such as the organic solvent mentioned by the term of the above-mentioned cationic liquid constituent and other additives, for example, a viscosity controlling agent, pH regulator, antiseptics, various surface active agents, an anti-oxidant, an evaporation accelerator, a water-soluble anionic compound, and binder resin, may be blended suitably. Moreover, as mentioned later, it is a desirable gestalt in the preservation stability of a liquid constituent and ink to add a photopolymerization initiator and a sensitizer in a liquid constituent at the same time it promotes hardening of a monomer efficiently.

[0117] (Surface tension of a liquid constituent) The anionic liquid constituent of this invention may be toned according to the color of recorded media, although it is more desirable to be colorlessness or that it is white. Furthermore, as suitable range of the various physical

properties of the above liquid constituents, surface tension is more preferably made into 10 – 40 mN/m (dyn/cm) ten to 60 mN/m (dyn/cm), and viscosity is made into 1 – 30 mPa·s (cP).

[0118] (The manufacture approach of a liquid constituent) As the manufacture approach of the liquid constituent of this invention containing the aforementioned cationicity or an anionic particle, it can choose suitably from the approaches generally used for distribution, and can use. In order to make the mean particle diameter and particle size distribution of a particle in a liquid constituent into the above-mentioned range, using dispersers, such as a roll mill, a sand mill, a homogenizer, an ultrasonic homogenizer, and extra-high voltage emulsifiers (for example, trade name nano mizer etc.), the classification processing by distributed processing, centrifugal separation, ultrafiltration, etc. is used suitably, and, specifically, can arrange the diameter of a particulate material of the particle in a liquid constituent with these processing means.

[0119] Energy grant explains a polymerization and the polymerization nature component (monomer) which constructs a bridge as an indispensable component contained in <water-color-ink> ink.

[0120] (Polymerization nature component) – ink in this invention contains the solvent which dissolves the polymerization nature component (monomer) and this monomer which are converted into the cross linked polymer by grant of energy other than the color material mentioned later as an indispensable component. The purpose using this monomer sticks the coloring section with recorded media, is enclosing color material by the crosslinked polymer formed of the energy grant to a monomer with the particle, and is to raise the scratch-proof nature and weatherability of the coloring section while making the coloring section form on the scarce recorded media of absorbency, such as a plastics metallurgy group, at stability as the term of a mechanism described. In addition, in this invention, a monomer may call it hardening a polymerization and to construct a bridge and to convert into the cross linked polymer by energy grant.

[0121] As a monomer hardened by grant of the energy used for the liquid constituent of this invention, the acrylic (meta) monomers of radical polymerization nature and the epoxy monomers which suit a cationic polymerization system can use it suitably. As acrylic (meta) monomers of radical polymerization nature, the following monomer is mentioned, for example.

[0122] Specifically (1) N and N-dimethylaminoethyl methacrylate $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (2) N, N-dimethylamino ethyl acrylate $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (3) 2 N, N-dimethylaminopropyl methacrylate $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (4) N, NN[– dimethylaminopropylacrylate $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$] (5) 2 N, N-dimethylamino acrylamide $\text{CH}_2=\text{CH}-\text{CON}(\text{CH}_3)_2$ (6) 2 N, and N-dimethylamino meta-acrylamide $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CON}(\text{CH}_3)_2$ (7) N, N-dimethylaminoethyl acrylamide $\text{CH}_2=\text{CH}-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2$ (8) N, N-dimethylaminoethyl meta-N[acrylamide $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2$] (9) 2 N, N-dimethylaminopropyl acrylamide $\text{CH}_2=\text{CH}-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2$ (10) N, N-dimethylaminopropyl methacrylamide $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2$, these monomers formed into 4 class Color-material dyeing property, It excels in the film strength and is especially desirable.

[0123] Moreover, the well-known ultraviolet curing mold monomers and the oligomer of the acrylic ester (meta) of polyhydric alcohol, the acrylic ester (meta) of the glycidyl ether of polyhydric alcohol, the acrylic ester (meta) of a polyethylene glycol, the acrylic ester (meta) of the ethylene oxide addition product of polyhydric alcohol, and a polybasic acid anhydride and hydroxyl-group content (meta) acrylic ester, such as a reactant, are used. The high matter of the compatibility in the inside of a liquid constituent out of these monomers or a hydrophilic property is chosen, and it is used. As epoxy monomers which suit a cationic polymerization system, the glycidyl ether of polyhydric alcohol, glycidyl ester, aliphatic series annular epoxide, etc. are used, for example.

[0124] In this invention, when a pigment is used especially for ink as a color material and ultraviolet rays are used as hardening energy, the cure rate of a monomer tends to become slow. Therefore, as a polymerization system of a (ultraviolet-rays UV) polymerization monomer, the monomer of a high Brit polymerization system is desirable, and, subsequently to order, it is desirable to select the monomer of a cationic polymerization system and a free radical polymerization system.

[0125] The content of the monomer contained in the liquid constituent in this invention usually has the desirable range of 1 – 50 mass %. The hardenability of under 1 mass % is inadequate, and since the viscosity of a constituent will rise and dischargeability will worsen if weatherability, solvent resistance, scratch-proof nature, and adhesion will become low and 50 mass % is exceeded, a generation polymer is not desirable. It is three to 40 mass % preferably, and is choosing a monomer in this range, and in this range, there is an advantage that the liquid constituent which is compatible in hardenability and dischargeability is obtained, and it is five to 30 mass % still more preferably, and since dischargeability is also satisfactory, it has [hardenability is enough, and] the advantage to which the selectivity of a monomer spreads.

[0126] (A photopolymerization initiator and sensitizer) When using ultraviolet-rays energy for hardening of the monomer in ink in this invention, it is desirable to use a photopolymerization initiator. As a photopolymerization initiator, a carbonyl compound, an azo compound, organic peroxide, etc. are mentioned, for example. as a usage — a photopolymerization initiator — one kind — or even if it uses two or more kinds, it does not matter even if it uses a photopolymerization initiator and a sensitizer together. It is not restricted especially that what is necessary is just to select suitably about selection of the main photopolymerization initiators and sensitizers, combination, and a compounding ratio with the ultraviolet-rays polymerization nature monomer and the equipment used to be used.

[0127] As main photopolymerization initiators, for example, acetophenone, 2, and 2-diethoxy acetophenone, p-dimethylamino acetophenone, p-dimethylamino propiophenone, A benzophenone, 2-chlorobenzo phenon, p, and p'-dichloro benzophenone, A p and p'-bis-diethylamino benzophenone, a Michler's ketone, benzyl (diphenyl diketone), A benzoin, benzoin methyl ether, benzoin ethyl ether, Benzoin iso-propyl ether, the benzoin-n-propyl ether, Benzoin isobutyl ether, benzoin-n-butyl ether, Benzyl dimethyl ketal, tetramethylthiuram monosulfide, Thioxanthone, 2-chloro thioxanthone, 2-methylthioxanthone, Azobisisobutyronitril, benzoin peroxide, G tert-butyl peroxide, 1-hydroxy cyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenyl-1-ON, 1-(4-isopropyl phenyl)-2-hydroxy-isobutane-1-ON, a methyl benzoyl FO mate, etc. are mentioned. The amount of these photopolymerization initiators used is usually 0.1 to 10 mass % to the total amount of an ultraviolet-rays hardenability monomer.

[0128] Moreover, in a cationic polymerization mold, photoinitiators, such as aromatic series diazonium salt, an aromatic series halo NIUMU salt, aromatic series sulfonium salt, and a metallocene compound, are used. Triphenylsulfonium hexafluoro phosphate, diphenyliodonium hexafluoroantimonate, etc. are mentioned as the example. Moreover, in the case of a cationic polymerization mold, in order to make hardening still more perfect, it is the range of 80–170 degrees C, and it is desirable to heat in 100–150 degrees C desirably especially. Although heating time changes with conditions, it is usually for 5 – 30 minutes.

[0129] The amine which contains 1. amine system:fatty amine and an aromatic series radical as a sensitizer, for example, A piperidine, 2. urea:allyl compound system, o-tolyl thiourea, 3. sulfur compound : Sodium diethyl dithiophosphate, A fusibility salt [of an aromatic series sulfinic acid], 4. nitril system compound:N, and N-JI permutation-p-amino benzonitrile, 5. — phosphorus-compounds: — tri-n-butyl phosphine and NETORIUMU diethyl JICHIOHOSU feed — 6. — nitride: — a Michler's ketone and N-NITORISO hydroxylamine derivative — An oxazolidine compound, tetrahydro – 1, 3-oxazine compound, Formaldehyde or an acetaldehyde, the condensate of diamine, 7. chlorine compound: A carbon tetrachloride, hexachloroethane, the macromolecule-ized amine of the resultant of 8. epoxy resin and an amine, a triethanolamine thoria chestnut rate, etc. are mentioned.

[0130] Although the above-mentioned photopolymerization initiator and a sensitizer can be included in both a liquid constituent, or both [either or], since the preservation stability of a liquid constituent becomes still higher by making it contain in an ink side and making it dissociate with a monomer especially, they are desirable. When using an electron ray as hardening energy, especially the above-mentioned photopolymerization initiator or the above-mentioned sensitizer are not needed. Moreover, there is also no exposure inhibition by the pigment, and since [with few temperature rises] a cure rate is also quick, as the hardening approach of the monomer of this invention, it is effective.

[0131] [Anionic ink], next the water anionic ink which constitutes the ink set of this invention combining the cationic liquid constituent explained by the above are explained. Combination with at least one sort of anionic ink in which an ink set here contains the liquid constituent and anionic matter (anionic color material) of this invention is said. Moreover, the combination of at least one kind of ink except the liquid constituent of this invention is called an ink subset from this ink set.

[0132] When using a pigment as a color material, using the water soluble dye which contains an anionic radical as a color material, as for the anionic ink used by this invention, it is desirable to use the thing (for this to also be called anionic color material by this invention) which made the anionic compound use together. Water, a water-soluble organic solvent and other components, for example, a viscosity controlling agent, pH regulator, antiseptics, a surfactant, an antioxidant, etc. are further contained and constituted by the above anionic ink used by this invention at this if needed. Hereafter, each constituent of these ink is explained.

[0133] (Water soluble dye) As water soluble dye which has the anionic radical used by this invention, especially if it is the water-soluble acid dye indicated by the Color Index (it may abbreviate to C.I. below by Color Index:), direct dye, and reactive dye, it will not be limited, for example. Moreover, what does not have a publication in a Color Index will not be limited especially if it has an anionic radical, for example, a sulfone radical, a carboxyl group, etc. A thing with the pH dependency of solubility is also contained in water soluble dye here.

[0134] (Pigment) You may be ink which uses a pigment and an anionic compound and contains water, a water-soluble organic solvent and other components, for example, a viscosity controlling agent, pH regulator, antiseptics, a surfactant, an antioxidant, etc. as another gestalt of water anionic ink instead of the water soluble dye which has the above anionic radicals if needed. Here, an anionic compound may be the dispersant of a pigment, and when the dispersant of a pigment is not anionic, what added the anionic compound different from a dispersant may be used. Of course, even when a dispersant is an anionic compound, what added the anionic compound of further others may be used.

[0135] Although there is especially no limitation in the pigment which can be used by this invention, the pigment explained below can use it suitably, for example. First, as carbon black used for black pigment ink, it is carbon black manufactured with the furnace method or the channel process, and that in which 40-150ml / 100g, and volatile matter have 0.5 to 10 mass %, and a pH value has [a specific surface area according / primary particle size / to 15 - 40mmum and a BET adsorption method / 50-300m²/g and DBP oil absorption] 2-9 is desirable.

[0136] As such a thing, they are No.2300, No.900, MCF88, No.40, No.52, MA7 and MA8, and No.2200B (above), for example. Mitsubishi Chemical make : RAVEN 1255(made in Colombia):REGAL 400R, REGAL 660R, MOGUL L (above) Cabot make: Color Black FW1, Color Black FW18, Color Black S 170, Color Black S 150, Printex 35, Printex U (above) Commercial items, such as the Degussa make, can be used. Moreover, a prototype could newly because of this invention be built.

[0137] As a pigment used for yellow ink, it is C.I.Pigment Yellow, for example. 1, C.I.Pigment Yellow 2, C.I.Pigment Yellow 3, C.I.Pigment Yellow 13, C.I.Pigment Yellow 16, and C.I.Pigment Yellow 83 grade are mentioned.

[0138] As a pigment used as Magenta ink, C.I.Pigment Red 5, C.I.Pigment Red 7, C.I.Pigment Red 12, and C.I.Pigment Red 48(calcium) C.I.Pigment Red 48 (Mn) and C.I.Pigment Red 57(calcium) C.I.Pigment Red112 and C.I.Pigment Red 122 grade are mentioned, for example.

[0139] As a pigment used as cyanogen ink, it is C.I.Pigment Blue, for example. 1, C.I.Pigment Blue 2, C.I.Pigment Blue 3, C.I.Pigment Blue 15:3, C.I.Pigment Blue 16, C.I.Pigment Blue 22, C.I.Vat Blue 4, and C.I.Vat Blue 6 grade are mentioned. moreover, the above — what was newly manufactured also about the color material of which color for this invention is usable.

[0140] (Pigment agent) Anythings are usable if it is water soluble resin which has the function to make water or an aquosity medium distribute a pigment to stability, by existence of an anionic radical as a dispersant of the pigment which can be used for the ink used by this invention. Especially, the thing of the range of 1,000-30,000 has desirable weight average molecular weight. Furthermore, the range of weight average molecular weight is 3,000-15,000 preferably. The salt

of the block copolymer which specifically consists of two or more monomers chosen from a hydrophobic monomer or an acrylic acid, an acrylic-acid derivative, a maleic acid, a maleic-acid derivative, an itaconic acid, an itaconic-acid derivative, a fumaric acid, and fumaric-acid derivatives, such as fatty alcohol ester of styrene, styrene derivative, vinyl naphthalene, vinyl naphthalene derivative, alpha, and beta-ethylene nature unsaturated carboxylic acid, a graft copolymer, random copolymers, or these (**) polymers etc. is mentioned. These resin is resin of an alkali meltable mold meltable in the water solution in which the base was dissolved.

[0141] Furthermore, the homopolymers which consist of a hydrophilic monomer, or those salts are sufficient. Moreover, it is also possible to also use water soluble resin, such as polyvinyl alcohol, a carboxymethyl cellulose, and a naphthalene sulfonic-acid formaldehyde condensate. However, the direction at the time of using the resin of an alkali meltable mold is possible for hypoviscosity-izing of dispersion liquid, and there is an advantage that distribution is also easy. As for said water soluble resin, it is desirable to be used in the range of 0.1 – 5 mass % to the ink whole quantity.

[0142] In the pigment and water soluble resin like ****, in a water-soluble medium, it distributes or dissolves and the pigment ink which can be used by this invention is constituted. In the pigment ink which can be used for this invention, it is the mixed solvent of water and a water-soluble organic solvent as a suitable aqueous medium, and it is desirable to use not the common water that contains various ion as water but ion exchange water (deionized water).

[0143] When a dispersant is not an anionic macromolecule, it is desirable to add an anionic compound further in the ink containing the pigment mentioned above. The anionic surfactant of low molecular weight which is listed to the following besides high polymers, such as alkali fusibility resin explained by the term of a pigment agent, as an anionic compound suitably used by this invention can be mentioned.

[0144] As the anionic surfactant of low molecular weight being concrete For example, sulfo succinic-acid lauryl disodium, sulfo succinic-acid polyoxyethylene lauroyl ethanol AMIDOESUTERU disodium, Polyoxyethylene alkyl sulfo succinic-acid disodium, carboxylation polyoxyethylene lauryl ether sodium salt, Carboxylation polyoxyethylene tridecyl ether sodium salt, Although polyoxyethylene lauryl ethereal sulfate sodium, polyoxyethylene lauryl ethereal sulfate triethanolamine, a polyoxyethylene-alkyl-ether sodium sulfate, sodium alkylsulfate, alkyl-sulfuric-acid triethanolamine, etc. are mentioned It is not limited to these. The suitable amount of the above anionic matter used is the range of 0.05 – 10 mass % to the ink whole quantity, and is 0.05 to 5 mass % still more suitably.

[0145] (Self-distributed pigment) As a pigment which can be used for anionic ink, the pigment of self-distributed process input output equipment which water or an aqueous medium can be made to distribute can also be used again, without using a dispersant. As for the pigment of self-distributed process input output equipment, at least one sort of anionic hydrophilic radicals are combined with the pigment front face through direct or other atomic groups. The naphthylene radical on which at least one sort chosen from the next hydrophilic radicals as an anionic hydrophilic radical, for example and the atomic group of further others may have the phenylene group which may have the alkylene group of the carbon atomic numbers 1–12 and a substituent, or a substituent is mentioned.

– COOM, –SO₃M, –SO₂NH₂, –PO₃HM, –PO₃M₂ (M in the above-mentioned formula expresses a hydrogen atom, alkali metal, ammonium, or organic ammonium.)

[0146] Thus, since the pigment which electrified anionic by installation of the hydrophilic radical on the front face of a pigment has water-dispersion [which was excellent with repulsion of ion], it maintains the distributed condition stabilized even if it did not add a dispersant etc., also when it was made to contain in water color ink. It is desirable when especially a pigment is carbon black.

[0147] (Addition component in ink) In order to consider as the ink which has a desired physical-properties value other than the above-mentioned component if needed again, a surfactant, a defoaming agent, or antiseptics can be added in ink, and commercial water soluble dye etc. can also be added further.

[0148] As a surfactant, nonionic surfactants, such as anionic surfactants, such as fatty-acid

salts, higher-alcohol sulfate salts, liquid fatty-oil sulfate salts, and alkyl allyl compound sulfonates, polyoxyethylene alkyl ether, polyoxyethylene alkyl ester, polyoxyethylene sorbitan alkyl ester, acetylene alcohol, and an acetylene glycol, are mentioned, and these one sort or two sorts or more can be used, for example, choosing them suitably. Although the amount used changes with additions of a dispersant, its 0.01 – 5 mass % is desirable to the ink whole quantity. Under the present circumstances, it is desirable to determine the addition of a surfactant that the surface tension of ink will become more than 30 mN/m (dyn/cm). In the ink jet recording method used by this invention, it is because generating of the printing kink (gap of the impact area of an ink droplet) at the tip of a nozzle depended for getting wet can be suppressed effectively.

[0149] After adding and stirring a pigment first as the production approach of pigment ink which was explained above in the water solution which contains the resin for pigment-content powder, and water at least, for example, distributed processing is performed using the below-mentioned distributed means, centrifugal separation processing is performed if needed, and desired dispersion liquid are obtained. Next, what is necessary is to add further a component which was hung up over these dispersion liquid above, to stir it, and just to consider as ink.

[0150] Moreover, in using the resin of an alkali meltable mold, in order to dissolve resin, it requires adding a base. Under the present circumstances, the amine for dissolving resin or the amount of a base needs to add 1 or more times of the amine called for by count from the acid number of resin, or the amount of bases. The amount of an amine or a base is calculated by count by the following formulas.

アミン或いは塩基の量 (g)

$$= \frac{(\text{樹脂の酸価} \times \text{アミン或いは塩基の分子量} \times \text{樹脂量 (g)})}{5600}$$

[0151] Furthermore, if pre mixing is performed more than for 30 minutes before carrying out distributed processing of the water solution containing a pigment, the distributed effectiveness of a pigment will become good. This pre mixing actuation improves the wettability on the front face of a pigment, and promotes adsorption of the dispersant on the front face of a pigment.

[0152] As bases added by the dispersion liquid at the time of using alkali meltable mold resin, it is desirable to, use inorganic bases, such as organic amines, such as monoethanolamine, diethanolamine, triethanolamine, amine methyl propanol, and ammonia, or a potassium hydroxide, and a sodium hydroxide, for example.

[0153] On the other hand, although what kind of thing may be used if the disperser used for preparation of pigment ink is a disperser generally used, a ball mill, a sand mill, etc. are mentioned, for example. Also in it, the sand mill of a high-speed mold is desirable, for example, a super mill, a Sand grinder, a bead mill, an agitator mill, a grain mill, a die Norian mill, a pearl mill, the COBOL mill (all are trade names), etc. are mentioned.

[0154] [Cationic ink], next the water cationic ink which constitutes the ink set of this invention combining the anionic liquid constituent explained previously are explained. Combination with at least one sort of ink in which an ink set here contains the liquid constituent and cationic matter (cationic color material) of this invention is said. Moreover, the combination of at least one sort of ink except the liquid constituent of this invention is called an ink subset from this ink set. When using a pigment as a color material as a color material, using the water soluble dye containing a cationic radical, as for the cationic ink used by this invention, it is desirable to make a cationic compound use together (for this concomitant use to also be called cationic color material in this invention). Water, a water-soluble organic solvent and other components, for example, a viscosity controlling agent, pH regulator, antiseptics, a surfactant, an antioxidant, etc. are further contained and constituted by the above ink used by this invention at this if needed. Hereafter, each constituent of these ink is explained.

[0155] (Water soluble dye) As water soluble dye which has the cationic radical used by this invention, especially if it is the water-soluble color indicated by the Color Index, it will not be limited, for example. Moreover, if what does not have a publication in a Color Index has a cationic radical, there will be especially no limitation. In addition, a thing with the pH dependency of

solubility is also contained in water soluble dye here.

[0156] (Pigment) You may be ink which uses a pigment and a cationic compound and contains water, a water-soluble organic solvent and other components, for example, a viscosity controlling agent, pH regulator, antiseptics, a surfactant, or an antioxidant if needed instead of the water soluble dye which has the above-mentioned cationic radical as another gestalt of the ink used by this invention. Here, a cationic compound may be the dispersant of a pigment, and when the dispersant of a pigment is not cationicity, what added the cationic compound different from a dispersant may be used. Of course, even when a dispersant is a cationic compound, the cationic compound of further others may be added. As a pigment which can be used by this invention, there is especially no limitation and it can use suitably the pigment stated by the term of anionic ink.

[0157] (Pigment agent) Anythings [its] are usable if the dispersant of the pigment in the ink used by this invention is water soluble resin which has the function to make water or an aqueous medium distribute a pigment to stability by existence of a cationic radical. Some polymers [at least] which are obtained by the polymerization of a vinyl monomer and are obtained as an example should just have cationicity. As a cationic monomer for constituting a cationic part, the salts and these compounds formed into 4 class of the tertiary amine monomer like the following are mentioned.

[0158] Specifically N and N-dimethylaminoethyl methacrylate $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]$, N and N-dimethylamino ethyl acrylate $[\text{CH}_2=\text{CH}-\text{COO}-\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]$, N and N-dimethylaminopropyl methacrylate $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$, N and N-dimethylaminopropylacrylate $[\text{CH}_2=\text{CH}-\text{COO}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$, N,N-dimethylacrylamide $[\text{CH}_2=\text{CH}-\text{CON}(\text{CH}_3)_2]$, N and N-dimethyl methacrylamide $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{CON}(\text{CH}_3)_2]$, N and N-dimethylaminoethyl acrylamide $[\text{CH}_2=\text{CH}-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2]$, N and N-dimethylaminoethyl methacrylamide $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2]$, N,N-dimethylaminopropyl acrylamide $[\text{CH}_2=\text{CH}-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$, N, and N-dimethylaminopropyl methacrylamide $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$

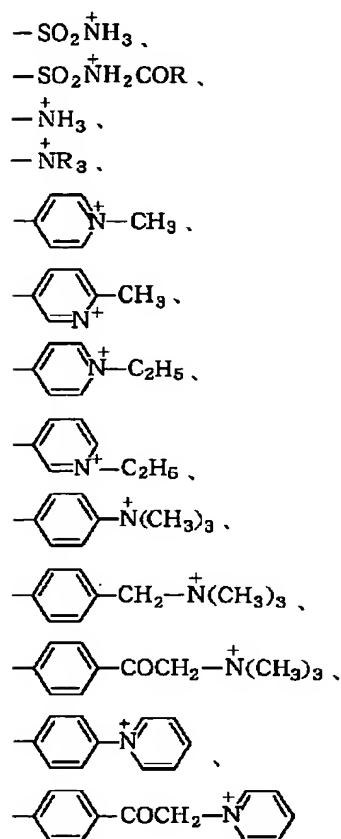
** is mentioned.

[0159] As a compound for forming a salt in the case of a tertiary amine monomer, a hydrochloric acid, a sulfuric acid, an acetic acid, etc. are mentioned, and a methyl chloride, a dimethyl sulfate, benzyl chloride, epichlorohydrin, etc. are mentioned as a compound used for the 4th class-ization, for example. Also in these, when a methyl chloride, a dimethyl sulfate, etc. prepare the dispersant used by this invention, it is desirable. Underwater, the salt or the 4th class ammonium compound of the above tertiary amine monomers is served as a cation, and acidity is a stable dissolution field on the neutralized conditions. The content in the inside of the copolymer of these monomers has the desirable range of 20 - 60 mass %.

[0160] In addition to this as a monomer, acrylamides, vinyl ether, vinyl pyrrolidone, vinylpyridines, and vinyl oxazoline are mentioned as a water-soluble monomer which can be dissolved in hydrophobic monomers, such as acrylic ester which has hydroxy groups, such as acrylic ester which is used for the configuration of the above-mentioned giant-molecule dispersant, and which has 2-hydroxyethyl methacrylate and a long-chain ethylene oxide chain in a side chain, for example, and a styrene system monomer, and with a pH of about seven water. As a hydrophobic monomer, hydrophobic monomers, such as styrene, a styrene derivative, vinyl naphthalene, a vinyl naphthalene derivative, alkyl ester of an acrylic acid (meta), and acrylonitrile, are used. In order that a water-soluble monomer may make a copolymer exist in stability in a water solution in the macromolecule dispersant obtained by copolymerization, it uses in the range of 15 - 35 mass %, and in order to heighten the dispersion effect over the pigment of a copolymer, as for a hydrophobic monomer, it is desirable to use in the range of 20 - 40 mass %.

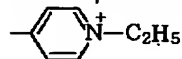
[0161] (Self-distributed pigment) In the case of the pigment charged in cationicity, that with which the hydrophilic radical combined through direct or other atomic groups combined at least one chosen from the next 4th class ammonium is mentioned. However, this invention is not limited to these.

[0162]



[0163] R expresses the naphthyl group which is not permuted [the phenyl group which is not permuted / the shape of a straight chain of the carbon atomic numbers 1-12, a branched-chain alkyl group, a permutation, or /, a permutation, or] among the above-mentioned formula. In addition, for example, NO_3^- and CH_3COO^- exist in the above-mentioned cationic radical as counter ion.

[0164] If it explains taking the case of the approach of combining N-ethyl pyridyl radical of the structure shown below, for example as an approach of manufacturing the self-distributed pigment which a hydrophilic radical which was described above was combined and has been charged in cationicity, the method of processing a pigment with a 3-amino-N-ethyl pyridinium star's picture will be mentioned.



[0165] Thus, since the pigment which electrified cationicity by installation of the hydrophilic radical on the front face of a pigment has water-dispersion [which was excellent with repulsion of ion], it maintains the distributed condition stabilized even if it did not add a dispersant etc., also when it was made to contain in water color ink. The case where especially the above-mentioned pigment is carbon black is desirable.

[0166] The cationic ink further used by this invention is adding said surfactant from the field which makes good the permeability of the ink to recorded media, and matching of as opposed to [get wet, simultaneously] the head for ink jets. (Surface tension of ink) It is desirable to adjust the surface tension in 25 degrees C to 30 - 68 mN/m (dyn/cm) as physical properties of ink itself, and to adjust viscosity to below 5 mPa-s (cP) more preferably below 10 mPa-s (cP) below 15 mPa-s (cP).

[0167] (Other components contained in ink) In addition, the ink used by this invention may add additives other than the above-mentioned component, such as a water-soluble organic solvent, a surface active agent, pH modifier, a rust-proofer, an antifungal agent, an antioxidant, an evaporation accelerator, a chelating agent, and a water-soluble polymer, if needed.

[0168] As for the solvent object which dissolves or distributes the above-mentioned monomer which can be used by this invention, it is desirable that it is the mixture of water and a water-soluble organic solvent. As a water-soluble concrete organic solvent, for example Methyl alcohol, ethyl alcohol, N-propyl alcohol, isopropyl alcohol, n-butyl alcohol, Alkyl alcohols of the carbon numbers 1-4, such as sec-butyl alcohol and tert-butyl alcohol : Dimethylformamide, amides [, such as dimethylacetamide,]: — ketones [, such as an acetone,]: — a tetrahydrofuran — Ether, such as dioxane : Polyalkylene glycols:ethylene glycol, such as a polyethylene glycol and a polypropylene GUKORI call, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, and 6-KISAN triol and thiodiglycol — passing — a xylene glycol — The alkylene glycol in which alkylene groups, such as a diethylene glycol, contain 2-6 carbon atoms : A glycerol, The low-grade alkyl ether of polyhydric alcohol, such as the ethylene glycol monomethyl (or ethyl) ether and the diethylene-glycol monomethyl (or ethyl) ether : A N-methyl-2-pyrrolidone, Imide compounds, such as cyclic amide compounds, such as 1,3-dimethyl-2-imidazolidinone, a sulfolane, dimethyl sulfoxide, 2-pyrrolidone, and epsilon caprolactam, and a succinimide, etc. are mentioned.

[0169] Generally, 1 - 40% of the content of the water-soluble above-mentioned organic solvent is desirable to the total mass of ink, and is 3 - 30% of range more preferably. Moreover, when it is made into the range of 30 - 95 mass %, the content of the water in ink is good, and since it can suppress that the viscosity of ink becomes high and can fully satisfy a fixing property, it is desirable. [of the solubility of color material]

[0170] Although the ink used by this invention can be used also as ink of common aquosity writing materials, especially when applying to the ink jet record approach of a type of making ink breathing out according to the foaming phenomenon of the ink by heat energy, it is suitable, and it becomes very stable [the regurgitation], and there is the description that generating of a satellite dot etc. does not arise. However, a thermal physical-properties value (for example, the specific heat, a coefficient of thermal expansion, thermal conductivity) may be adjusted in this case.

[0171] Although the concentration of the color-material component contained in the anionic and cationic ink of which the <concentration of water color ink> above was done is suitably chosen according to the class of color material, such as an aquosity color, a pigment, and a self-distributed pigment, 0.1 - 12% of its range is especially desirable 0.1 to 20% to the total mass of ink. Moreover, especially the color enhancement of the image with which the concentration of a color-material component is formed under the record conditions of the usual 2 liquid system when color material takes especially or less for 1.0 1.2 or less to this particle 1 on mass criteria, concerning the relation between the concentration of the particle in a liquid constituent and the concentration of the color material in ink in the range of 0.3 - 7 mass % becomes the outstanding thing.

[0172] The <approach of forming the coloring section in recorded media>, next the approach of forming the coloring section in the recorded media of this invention are explained. The approach of forming the coloring section in the recorded media of this invention (i) The solvent which dissolves the monomer and this monomer which carry out a polymerization by grant of color material and energy is included. It has the process which gives the liquid constituent which contains the particle to which the front face is charged in a polarity contrary to the process and (ii) this ink which give anionic or cationic ink to recorded media in the state of distribution to recorded media. It is characterized by giving ink and a liquid constituent to the front face of the above-mentioned recorded media so that it may touch in the state of a liquid mutually. How to give the liquid constituent and ink which are hereafter constituted as mentioned above on recorded media is explained.

[0173] The approach of forming the coloring section in the recorded media of this invention includes the process (i) containing the process (ii) which gives a liquid constituent which was explained above on recorded media, and the solvent which dissolves the monomer and this monomer which carry out a polymerization by grant of color material and energy which gives anionic or cationic ink to recorded media. Although a liquid constituent is given to the coloring section formation field of the recorded media formed in the ink which contains color material in

that case or a coloring section formation field, and its near, ink and a liquid constituent are given so that they may touch in the state of a liquid mutually. A coloring section formation field here is a field where the dot of ink adheres, and the thing of the field which about 1-5 dots of outsides of the field where the dot of ink adheres left is pointed out near the coloring section formation field.

[0174] As long as it is the approach the above mentioned liquid constituent and the ink of this invention come to touch the recorded media of this invention in the state of a liquid mutually on recorded media by the approach of forming the coloring section, these may be made to give by which approach. Therefore, it is not a problem any shall be previously given on recorded media between a liquid constituent and ink. For example, after performing a process (i) after performing a process (ii), and performing a process (i), ***** is also good in a process (ii). Moreover, after performing a process (i), it is also desirable to perform a process (ii) and to perform a process (i) again after that. Moreover, when a liquid constituent is made to give previously recorded media, it is not restricted especially about time amount after giving a liquid constituent to recorded media until it makes ink give on recorded media, but in order to make it touch in the state of a liquid mutually, it is desirable to make ink give within coincidence or several seconds on recorded media mostly.

[0175] Next, also about the timing which gives the energy which stiffens the monomer in ink, if it is after giving the both sides of ink and a liquid constituent, it can choose freely [always]. However, after forming the pixel of the last liquid constituent, it is necessary to surely give energy and to harden a monomer. Moreover, when giving energy about removal of the solvent in a liquid constituent and ink, i.e., desiccation, it is desirable that almost all solvents are removed. As a desiccation means, it is desirable to put a base material (recorded media) into an air-heating furnace with a temperature of about 50-200 degrees C. However, the polymerization of a monomer etc. may be performed in the condition of not removing a solvent from the purpose of compaction of the processing time completely, and you may dry later. Anyway, since the good thing of image physical properties is not obtained, it is not desirable that the solvent remains in the last image formation object. Moreover, as for the energy grant as a means to harden a monomer, UV irradiation, electron beam irradiation, heat radiation, etc. are mentioned as mentioned above. For example, it is desirable to irradiate about two 200 - 1000 mJ/cm ultraviolet rays in addition, using a high pressure mercury vapor lamp as a UV irradiation means. The range of the emission spectrum of the ultraviolet-rays field of the mercury lamp of the above-mentioned high pressure mercury vapor lamp is 184nm - 450nm, and it is suitable for stiffening an ultraviolet-rays hardenability monomer efficiently. Moreover, when using electron-beam-irradiation equipment, it is desirable to irradiate in the range of 1 - 50Mrad.

[0176] (Recorded media) Especially the recorded media used for the approach of forming the coloring section in the recorded media of above-mentioned this invention are not limited, and various objects, such as the so-called regular papers, such as a copy paper currently used from the thing of the absorbency scarce quality of the materials, such as art paper for printing, plastics, a metal, and a tile, and the former and bond paper, are used suitably. Of course, the coat paper and the bright film for OHP which were specially produced to ink jet record are also used suitably. Furthermore, common paper of fine quality and glossy paper can also be used suitably.

[0177] (The grant approach of a liquid constituent) Although how to make it give all over recorded media with a spray, a roller, etc. is also considered, for example as an approach of making the liquid constituent of this invention give on recorded media Furthermore, it is desirable alternative only near the coloring section formation field which gives ink preferably or a coloring section formation field, and its coloring section formation field, and that the ink jet method which can make a liquid constituent give homogeneity performs. Moreover, although various ink jet recording methods can be used in this case, especially a desirable thing is a method which carries out the regurgitation of the drop using the air bubbles generated with heat energy.

[0178] A <ink jet recording apparatus>, next the ink jet recording apparatus of this invention are explained. The ink hold section in which the ink jet recording device of this invention contains the solvent which dissolves the monomer and this monomer which carry out a polymerization by

grant of color material and energy and which held anionic or cationic water color ink, It is characterized by having the 1st record unit equipped with the ink jet head which makes this ink breathe out, the liquid constituent hold section which held the liquid constituent of said this invention, and the 2nd record unit equipped with the ink jet head which makes this liquid constituent breathe out.

[0179] Especially the ink jet recording device that can be used for the ink jet record approach of this invention It is the ink jet recording device which gives a liquid constituent and the ink of at least one or more colors from the recording head equipped with two or more ink deliveries also to recorded media without ink absorptivity, and forms a record image. a) The means which carries out defecation processing of said recorded-media front face, the recording head equipped with two or more ink deliveries which an ink droplet is made to fly according to b image recording signal, and give an ink droplet to the predetermined location on said front face of recorded media, and a means to stiffen the ink droplet of the c aforementioned image formation are provided.

[0180] In the ink jet recording device concerning this invention, the means of a may be omitted depending on recorded media. Moreover, as technique, UV/O₃ washing is mentioned, for example. As a hardening means of the ink droplet of c), a UV irradiation lamp, EB (electron ray) exposure, heat, etc. are mentioned. In a UV irradiation lamp, since heat may occur and recorded media may deform, it is desirable that a cooler style, for example, a cold mirror, a cold filter, work-piece cooling, etc. possess.

[0181] Drawing 1 is the typical schematic diagram showing the whole ink jet recording device. 110 in drawing 1 is a recording head, and is the ink jet recording head by which 300 nozzle x5 train of 600dpi was arranged together with one. As a liquid constituent and ink, five heads for four classification by color of Y (yellow), M (Magenta), C (cyanogen), and Bk (black) are prepared, and the above-mentioned recording head is set so that a full color image can be recorded by one scan. 101 is recorded media. The recorded media 101 of two or more sheets are set to the stocker 111, and it is sent to a band conveyor 113 by the conveyance machine 112, and is sent out to the tray 115 for printing. 114 is an auxiliary roller for sending recorded media.

[0182] Adsorption immobilization of the recorded media 101 sent to the tray 115 for printing is firmly carried out by suction with a pump 116 on a tray. The recorded media 101 on the tray 115 for printing are sent into the field to which the 1st processing process is performed. 104 is UV/O₃ lamp. With recorded media, when surface wettability is low, surface treatment of recorded media is performed and the wettability of ink and adhesion are raised. This processing process may be passed (abbreviation).

[0183] Shortly after recorded media are taken out from the field of the 1st process by the delivery motor of 111, ink jet record by the recording head 110 is performed. Although various ink jet recording methods, such as a piezo method and an electrostatic method, can be used for ink jet record which is this 2nd process, the bubble jet (trademark) method which is stabilized and can perform high-speed record is suitable.

[0184] Moreover, if it seems that problems, such as a blot, occur in one-pass printing also as the record approach, a two pass and 4 pass printing will be adopted. The recorded media with which the image was recorded are immediately conveyed to the field to which solidification of the 3rd process is performed. Here, 105 is a UV irradiation lamp.

[0185] Since heat occurs and deformation of recorded media may be caused by the exposure of UV lamp, heating prevention devices, such as a cold mirror, a cold filter, and work-piece air cooling (un-[in a Fig.] illustrating above), are required.

[0186] The recorded media (it has a record image) which passed through the above three processing processes are conveyed by the stocker 119 through a band conveyor 120 and the delivery roller 121, and are contained by the predetermined location with a handler 118.

[0187] In the illustrated example, although recorded media 101 are the thing of a tabular configuration, the tray which conveys this is suitably adjusted so that it can respond to the configuration of recorded media. For example, correspondence also in record to the disc-like recorded media 101 is attained by using spacer 211 grade as shown in drawing 3 . Moreover, as for this equipment, it is desirable to have a means to adjust the distance of a recording head and

the image formation side of recorded media according to the thickness of recorded media.

[0188] Moreover, in order to promote the heat hardening (bridge formation of a polymer) in the 1st process and 3rd process, by forming heating means, such as a heater, in a tray auxiliary, for example, heating recorded media before each processing, heating effectiveness is raised even to processing of comparatively large-sized recorded media with big heat capacity, and effective processing is attained.

[0189] In addition, when it heat-treats to recorded media, and deviation arises in a dimension, a gap of the cross direction of record and a feed direction arises and problems, such as generating of the white stripe in a record image and gap of printing size, arise by thermal expansion, as shown in drawing 4 It compares with the value beforehand set up with the comparator after detecting the skin temperature of the image formation side of recorded media 401 with the thermo sensor 402, amplifying with the amplifier (Amp) and digitizing this with an A/D converter (A/D). It is desirable to use the system adjusted so that recorded media can be set to a recording head 410 and a motor 403 by the optimal delay signal over the signal of a clock to a signal at delivery and a right location.

[0190] Moreover, in order to make recorded media convey with a sufficient precision, marking of the mark can be carried out to the non-printing area of recorded media with etching or a press, the location can be read with a suitable read means, the location of recorded media can always be checked, a conveyance means can be controlled by the location, and more accurate conveyance can also be performed. Moreover, when curvature etc. is in recorded media, it is also effective in a roller etc. to add the function which corrects curvature because of [, such as curvature,] amendment. Moreover, what is necessary is just to remove this with the means of a shirring press etc. after printing, if the aforementioned mark spoils product value.

[0191] Drawing 2 is the typical schematic diagram showing other whole recording device. 130 in drawing is the recording head of the type which gave the liquid constituent for every color of ink, for example, is the ink jet recording head of 300x600dpi2 trains. 130Y, 130M, 130C, and 130B are the recording heads which made one set one color each and liquid constituent of Y (yellow), M (Magenta), C (cyanogen), and B (black). For example, after printing yellow and a liquid constituent by 130Y, UV lamp of 105 performs UV irradiation and only UV which the front face of ink hardens at least is irradiated.

[0192] By the delivery motor of 111, the recorded media 101 on the conveyance tray 115 are conveyed to the place of the following ink jet recording head of 130M in order to print the following color. An ink front face is stiffened with the UV lamp 105 after printing. Then, a full color image is repeatedly formed with 130C and 130B. Other detailed explanation is the same as explanation of drawing 1.

[0193] Although drawing 1 and drawing 2 are performing UV irradiation after one color or 4 color printing, they may install a spot UV lamp beside an ink cartridge, and it may carry out UV irradiation for every one pass (un-illustrating).

[0194]

[Example] Next, an example and the example of a comparison are given and this invention is explained still more concretely. In addition, as long as there is no notice especially, there are mass criteria among a sentence with the "section" and "%."

[0195] First, production of the liquid constituent of this invention is explained. After carrying out the mixed dissolution of each component shown below, pressure filtration was carried out with the membrane filter (a trade name, a FURORO pore filter, Sumitomo Electric Industries make) whose pore size is 1 micrometer, and liquid constituent A-C of this invention was obtained.

[0196] (Synthetic example of hydrated alumina) Aluminum DODEKISHIDO was manufactured by the approach of a publication to U.S. Pat. No. 4,242,271. Next, by the approach indicated by U.S. Pat. No. 4,202,870, said aluminum DODEKISHIDO was hydrolyzed and the alumina slurry was manufactured. Water was added until the solid content of hydrated alumina became 8.2% about this alumina slurry. pH of an alumina slurry was 9.7. Added 3.9% of nitric-acid solution, adjusted pH to 5.3, it was made to ripe at 120 degrees with an autoclave for 7 hours, and the colloidal sol was obtained. The nitric acid adjusted this colloidal sol to pH=4.0, it condensed to 20% of solid content concentration, and the hydrated alumina slurry was produced. A front face is underwater

charged in plus and the hydrated alumina in this slurry shows cationicity. Moreover, when made ion exchange water dilute and distribute this hydrated alumina slurry, it was dropped on the collodion membrane, and the test sample was produced and having been observed with the transmission electron microscope, it was the particle of a monotonous configuration.

[0197] <A presentation of the liquid constituent A>, and a glycerol The 10.0 sections and a diethylene glycol The 7.5 sections and a hydrated alumina slurry The 50.0 sections and water After mixing the 32.5 section above-mentioned component for 30 minutes by 3000rpm in an emulsification disperser (TK ROBOMIKKUSU, product made from special opportunity-ized Industry), centrifugal separation processing (for 4000rpm and 15 minutes) was performed, the big and rough particle was removed, and it considered as the liquid constituent A.

[0198]

<液体組成物Bの組成>

- ・ 1. 5-ペンタンジオール 10.0部
- ・ エチレングリコール 7.5部
- ・ コロイダルジルコニアゾル (固形分濃度20%) 50.0部
- ・ 水 32.5部

After mixing the above-mentioned component for 30 minutes by 3000rpm in an emulsification disperser (TK ROBOMIKKUSU, product made from special opportunity-ized Industry), centrifugal separation processing (for 4000rpm and 15 minutes) was performed, the big and rough particle was removed, and it considered as the liquid constituent B. A front face is underwater charged in plus and the zirconia particle in this zirconia sol shows cationicity.

[0199] <A presentation of the liquid constituent C>, and a guru serine The 10.0 sections and a diethylene glycol The 7.5 sections and a hydrated alumina slurry The 50.0 sections and a photopolymerization initiator (IRGACURE 2959, Ciba-Geigy make) The 3.0 sections and water After mixing the 29.5 section above-mentioned component for 30 minutes by 3000rpm in an emulsification disperser (TK ROBOMIKKUSU, product made from special opportunity-ized Industry), centrifugal separation processing (for 4000rpm and 15 minutes) was performed, the big and rough particle was removed, and it considered as the liquid constituent C.

[0200] Above-mentioned liquid constituent A-C was measured by the following approach, and each property and the evaluation result were shown in Table 1.

1) After diluting a liquid constituent with ion exchange water so that it may become 0.1% about the solid content concentration of the mean-particle-diameter particle of a particle, the ultrasonic washing machine was made to distribute for 5 minutes, and dispersion reinforcement was measured using the electrophoresis light scattering photometer (Otsuka Electronic company make, ELS-8000: 25 degrees C of solution temperature, quartz cell use). It asked for mean particle diameter with the KYUMURANTO analysis method from dispersion reinforcement using attached software.

[0201] 2) It measured to pH liquid constituent using the pH meter meter (the Horiba, Ltd. make, caster knee pH meter D-14) at 25 degrees C of solution temperature.

3) After diluting a liquid constituent with ion exchange water so that the solid content concentration of a F-potential particle may become 0.1%, it measured with the F-potential measurement machine (the product made from BURUKKUHEBUN, BI-ZETA plus: 20 degrees C of solution temperature, acrylic cel use).

[0202] 4) After putting a tank shelf-life liquid constituent in an ink tank, standing preservation was carried out for one month at the 60-degree C thermostat, and the liquid nature of the liquid constituent in a tank and the dischargeability from a recording head were evaluated.

O : sedimentation is not mostly seen within a tank but regurgitation stability is also good.

x: Sediment remarkably within a tank and dischargeability is also unstable.

[0203]

表1

液体組成物	A	B	C
平均粒子径 (nm)	70	115	75
pH	4.1	3.9	3.8
ゼータ電位 (mV)	41	69	40
タンク保存性	○	○	○

[0204] Next, production of the ink subsets 1 and 2 used in the example and the example of a comparison of this invention is explained.

Each component shown in the <production of ink subset 1> following was mixed, and it stirred enough, and after the dissolution, pressure filtration was carried out with the FURORO pore filter (a trade name, Sumitomo Electric Industries make) whose pore size is 0.45 micrometers, black, yellow, a Magenta and each color ink of cyanogen, and Bk1, Y1, M1 and C1 were obtained, and combination which consists of these color ink was made into the ink subset 1.

[0205] [Black ink Bk1]

**C. I. direct black 195 The 2.5 sections and 2-pyrrolidone The 10.0 sections and glycerol The 5.0 sections and isopropyl alcohol The 4.0 sections and sodium hydroxide The 0.4 sections and acrylic monomer (*1) The 10.0 sections and water The 68.1 sections [0206] [Yellow ink Y1]

– Projet Fast Yellow 2 (product made from Zeneca) The 2.0 sections and C.I. direct yellow 86 The 1.0 sections and thiodiglycol The 8.0 sections and ethylene glycol The 8.0 sections and ASECHIRE Norian EH The 0.2 sections (the Kawaken chemicals company make)

– Isopropyl alcohol The 4.0 sections and acrylic monomer (*1) The 10.0 sections and water The 66.8 sections [0207] [Magenta ink M1]

– Projet Fast Magenta 2 (product made from Zeneca) The 3.0 sections and glycerol The 7.0 sections and urea The 7.0 sections and ASECHIRE Norian EH The 0.2 sections (the Kawaken chemicals company make)

– Isopropyl alcohol The 4.0 sections and acrylic monomer (*1) The 10.0 sections and water The 68.8 sections [0208] [Cyanogen ink C1]

**C. I. direct blue 199 The 3.0 sections and ethylene glycol The 7.0 sections and diethylene glycol The 10.0 sections and ASECHIRE Norian EH The 0.3 sections (the Kawaken chemicals company make)

– Acrylic monomer (*1) The 10.0 sections and water 69.7 section (notes) *1: Ethoxylation trimethylolpropane triacrylate (trade name A-TMPT-3EO, product made from New Nakamura Chemistry)

[0209] By each component shown in the <production of ink subset 2> following, pigment dispersion liquid were prepared and black ink Bk2 was produced using this. Furthermore, yellow, a Magenta and each pigment ink of cyanogen, and Y2, M2 and C2 were obtained using the same pigment dispersion liquid, and combination which consists of these pigment ink was made into the ink subset 2.

[0210] [Black ink Bk2]

(Production of pigment dispersion liquid)

– The styrene-acrylic-acid-ethyl-acrylate copolymer (acid-number 140, weight average molecular weight 5,000) 1.5 section and monoethanolamine The 1.0 sections and diethylene glycol The 5.0 sections and water The 81.5 sections [0211] The above-mentioned component is mixed, it warms at 70 degrees C with a water bath, and a pitch is dissolved completely. After adding the carbon black (MCF88, Mitsubishi Chemical make) 10 section and the isopropyl alcohol 1 section which were newly made by this solution as an experiment and performing pre mixing for 30 minutes, distributed processing was performed on condition that the following.

– Disperser : Sand grinder (product made from the Igarashi machine)

– Grinding media : a zirconium bead, and filling factor:50% of the diameter of 1mm and grinding media (volume ratio)

– Grinding time amount : centrifugal separation processing (for 12,000rpm and 20 minutes) was

performed further for 3 hours, the big and rough particle was removed, and it considered as dispersion liquid.

[0212] (Production of black ink Bk2) The above-mentioned pigment dispersion liquid were used, the component which has the following presentation ratio was mixed, the ink containing a pigment was produced, and this was made into black ink Bk2.

– The above-mentioned pigment dispersion liquid The 30.0 sections and glycerol The 10.0 sections and ethylene glycol The 5.0 sections and N-methyl pyrrolidone The 5.0 sections and ethyl alcohol The 2.0 sections and acrylic monomer The 10.0 sections (trade name NK ester A-200, product made from New Nakamura Chemistry)

– Water The 38.0 sections [0213] Pigment content yellow ink Y2 was prepared like preparation of black ink Bk2 except having replaced with the pigment yellow 74 the carbon black (MCF88, Mitsubishi Chemical make) 10 section used on the occasion of preparation of [yellow ink Y2] black ink Bk2.

[0214] Pigment content Magenta ink M2 was prepared like preparation of black ink Bk2 except having replaced with the pigment red 7 the carbon black (MCF88, Mitsubishi Chemical make) 10 mass section used on the occasion of preparation of [Magenta ink M2] black ink Bk2.

[0215] Pigment content cyanogen ink C2 was prepared like preparation of black ink Bk2 except having replaced with the pigment blue 15 the carbon black (MCF88, Mitsubishi Chemical make) 10 mass section used on the occasion of preparation of [cyanogen ink C2] black ink Bk2.

[0216] (An example 1 – example 6) It printed in the combination of the following table 2 using liquid constituent A–C of this invention obtained as mentioned above, and each color ink of the ink subsets 1 and 2. In addition, examples 1–4 performed electron beam irradiation immediately after desiccation for 5 minutes at 60 degrees C after printing. exposure conditions — current: — it carried out by 6mA, and a part for /and line speed:10m dosage:3Mrad. On the other hand, examples 5 and 6 performed UV irradiation immediately after desiccation for 5 minutes at 60 degrees C after printing. The exposure was performed by 10 J/cm². This was made into the examples 1–6 of this invention.

[0217]

表2

実施例	インクサブセット	液体組成物
1	1	A
2	2	A
3	1	B
4	2	B
5	1	C
6	2	C

[0218] In the formation approach of the coloring section of the examples 1–6 used combining liquid constituent A–C and the ink subsets 1 and 2 as mentioned above, it recorded on the PET film of 100-micrometer thickness. Moreover, as an ink JIETO recording device used on that occasion, the color picture was formed using the recording device shown in drawing 1. Under the present circumstances, point-struck the liquid constituent, carried out it, it was made to adhere on a film first, and ink was made to adhere after that. Immediately after printing, energy was given on the above-mentioned conditions, and you stiffened the record image, and made it established. It checked having hardened any example enough.

[0219] Specifically, evaluation-criteria (1) – (5) performed 3 pass fine printing which prints a printing area by three scans. At this time, the liquid constituent printed in the pixel location where the ink of either yellow, a Magenta, cyanogen and black is printed for every pass. That is, the OR of the yellow for every pass, a Magenta, cyanogen, and the printing data of black was used as printing data of a liquid constituent. In addition, there is especially no limit in the class of fine mask at the time of this fine printing, and since the well-known technique is available,

detailed explanation here is omitted.

[0220] The recording head used here has the recording density of 600dpi, and made it 9.6kHz of drive frequencies as drive conditions. The discharge quantity per dot when using the head of 600dpi used [constituent / yellow, a Magenta, cyanogen ink, and / liquid] the head of 30ng(s) per dot about 15ng(s) and black ink, respectively. In addition, these record conditions are the same through an example and the example of reference.

[0221] (Examples 1 and 2 of reference) It printed in the combination of the following table 3 only using each color ink of the ink subsets 1 and 2 obtained as mentioned above. In addition, the examples 1 and 2 of reference performed electron beam irradiation immediately after desiccation for 5 minutes at 60 degrees C after printing. exposure conditions — current: — it carried out by 6mA, and a part for /and line speed:10m dosage:3Mrad.

[0222]

表3

参考例	インクサブセット	液体組成物
1	1	なし
2	2	なし

[0223] The recording head used in the record (examples 1-2 of reference) using the above-mentioned liquid constituent C and the ink subsets 1 and 2 has the recording density of 600dpi, and made it 9.6kHz of drive frequencies as drive conditions. The discharge quantity per dot when using the head of 600dpi used [ink / yellow, a Magenta, and / cyanogen] the head of about 30 ng(s) per dot about about 15 ng(s) and black ink, respectively, and recorded on the case of examples 1-6, and these conditions.

[0224] [The evaluation approach and valuation basis] The following evaluation approach and the valuation basis estimated each record image obtained in above-mentioned examples 1-6 and examples 1 and 2 of reference. The result was shown in Table 4.

[0225] (The evaluation approach of a record image)

(1) The RGB color chart of a color-enhancing highly minute XYZ-CIELAB-RGB standard image (SHIPP) (editorial supervision: the highly minute standard image creation committee : Institute of Image Electronics Engineers of Japan issue) was printed using the printer, and the colorimetry of those color charts was carried out. By the approach indicated by this technical explanatory, color-enhancing evaluation calculated three-dimension-breadth (in a sentence, it is hereafter called the color-gamut volume) of color distribution, and compared. At that time, the image processing at the time of forming a printing image was made into the same conditions, and the colorimetry was measured on light source:D50 and visual field:2 degree conditions by GRETAG SUPEKUTORORINO after after [printing] 24-hour progress. The valuation basis was shown below. The ratio of each color-gamut volume of examples 5 and 6 to the examples 1 and 2 over the example 1 of reference, the examples 3 and 4 over the example 2 of reference, and the example 3 of reference was made into the valuation basis.

[0226] AA: A color-gamut volume ratio is 1.4 or more times.

A : a color-gamut volume ratio is less than 1.2 to 1.4 times.

B : a color-gamut volume ratio is less than 1.0 to 1.2 times.

C : a color-gamut volume ratio is less than 1.0 times.

[0227] (2) After printing yellow, a Magenta, cyanogen, and the solid image of black each color using the printer which carried out the homogeneous above, viewing estimated the homogeneity of a color about white MOYA and color nonuniformity. The bad, especially homogeneous color was made applicable to evaluation. The valuation basis is as follows.

A: Hardly generate white MOYA and color nonuniformity.

B: Although white MOYA and color nonuniformity can be seen along with the fiber of paper a little, it is level without a parenchyma top problem.

C: Along with the fiber of paper, white MOYA and color nonuniformity look remarkable.

[0228] (3) After printing yellow, a Magenta, cyanogen, and the solid image of black each color using the printer which carried out the stripe nonuniformity above, viewing estimated stripe

nonuniformity. The bad color of especially stripe nonuniformity was made applicable to evaluation. The valuation basis is as follows.

A: Hardly generate stripe nonuniformity.

B: Although the stripe nonuniformity for every head scan can be seen a little, it is level without a parenchyma top problem.

C: The remarkable white stripe nonuniformity for every head scan can be seen.

[0229] (4) Yellow, a Magenta, cyanogen, and the solid image of the ink of black each color were printed using the printer which carried out the scratch-proof nature above. It is JIS about the pencil degree of hardness of the record image 16 hours after printing. It measured according to K5400. What has the lowest degree of hardness was made applicable to evaluation.

[0230] (5) Yellow, a Magenta, cyanogen, and the solid image of the ink of black each color were printed using the printer which carried out the weatherproof above. 24 hours after printing, the ozone weather meter (Suga Test Instruments Co., Ltd. make) performed the record image, and the exposure test was performed whenever [tub internal temperature] on 40 degrees C, 55% of humidity in a tub, the ozone level of 3 ppm, and the conditions of exposure time 2 hours. deltaE of each color before and behind a trial was measured, and the following criteria estimated by making applicable to evaluation what has the most remarkable tint change.

A: Less than deltaE5

B: deltaE5 to less than ten

C: deltaE10 or more

[0231]

表4

	発色性	均一性	スジムラ	耐擦過性	耐候性
実施例1	AA	A	A	4H	A
実施例2	AA	A	A	4H	A
実施例3	A	A	A	4H	A
実施例4	A	A	A	4H	A
実施例5	AA	A	A	4H	A
実施例6	AA	A	A	4H	A
参考例1	B	B	B	4H	A
参考例2	B	B	B	4H	A

[0232]

[Effect of the Invention] As explained above, according to this invention, absorbcency scarce recorded media, such as a plastics metallurgy group, are also received especially. The color enhancement which was excellent in the coat paper average for ink jets, and the homogeneity of a color can obtain. There is little stripe nonuniformity of the solid image section, and the ink jet record image excellent also in the scratch-proof nature of a record image is obtained. And shelf life, the dependability in printing, the ink set that is excellent also in the dependability of specifically not producing the regurgitation stability or blinding from a recording head, the approach of forming the coloring section in recorded media, and an ink jet recording device are offered.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] About the technique of obtaining the image which was excellent in color enhancement and the homogeneity of a color in formation of a color picture, this invention is divided and relates to the approach and ink jet recording device which form the coloring section in the ink set using the liquid constituent and this which can be used using an ink jet recording method the the best for the image formation to the absorbency scarce recorded media of the art paper for printing, a plastics, a metal, etc., etc., and recorded media.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] The ink jet record approach makes ink fly, and records by making ink adhere to recorded media, such as paper. For example, according to the ink jet record approach of a method of making a drop breathing out by giving heat energy to ink and generating air bubbles, using an electric conversion object as a regurgitation energy supply means currently indicated in JP,61-59911,B, JP,61-59912,B, and JP,61-59914,B, high density multi-orifice-ization of a recording head can be realized easily, and high resolution and a high-definition image can be recorded at high speed.

[0003] By the way, as for the ink used for the conventional ink jet record approach, what uses water as a principal component and contains water-soluble high boilers, such as a glycol, for the purpose, such as desiccation prevention of the ink within a nozzle and blinding prevention of a nozzle, in this is common. Therefore, when it records on recorded media using such ink, problems, such as generating of the ununiformity image presumed not to acquire fixable [sufficient] or to be based on uneven distribution of the loading material in the recording paper front face as recorded media and a sizing compound, may be produced.

[0004] On the other hand, the demand which searches for image quality with high film photo and this level is strong also to the ink jet record object in recent years, and the technical demand to raising the image concentration of an ink jet record image, extending a color reproduction field, and raising the homogeneity of the color of a record object further is very high.

[0005] In order to plan stabilization of the ink jet record approach, and upgrading of the record object by the ink jet record approach under such circumstances, various proposals have been made until now. the porosity particle which the approach of carrying out coating of a filler or the sizing compound is proposed on the base paper front face of recorded media as one of the proposals about recorded media, for example, adsorbs color material as a filler — a base paper — coating — carrying out — this porosity particle — the technique which forms an ink absorbing layer is indicated. The coat paper for ink jets etc. is put on the market as recorded media using these techniques.

[0006] In order to plan stabilization of the ink jet record approach, and upgrading of the record object by the ink jet record approach under such circumstances, various proposals have been made until now. Some of the typical thing is summarized to below.

(1) How to carry out internal [of a volatile solvent or the osmosis solvent] to ink : the approach of adding the compound which raises the permeability of a surfactant etc. to JP,55-65269,A into ink as a means which brings forward fixable [of the ink to recorded media] is indicated. Moreover, using for JP,55-66976,A the ink which made the volatile solvent the subject is indicated.

(2) How to mix ink and the liquid constituent which reacts on recorded media in ink : the approach of giving the liquid constituent which cheats out of an image good on recorded media after injection in advance of improvement in image concentration, waterproof improvement, and injection of the ink for forming a record image for the purpose of control of bleeding further is proposed.

[0007] for example, to JP,63-60783,A After making the liquid constituent containing a basic polymer adhere to recorded media, the approach of recording in the ink containing an anion color

is indicated. To JP,63-22681,A The record approach which mixes the second liquid constituent containing the compound which causes the 1st liquid constituent, these reactant chemical species, and reaction including reactant chemical species on recorded media is indicated. Furthermore, after giving the liquid constituent containing the organic compound which has two or more cationic radicals per molecule on recorded media, the approach of recording in the ink containing an anion color is indicated by JP,63-299971,A. Moreover, after giving the acid liquid constituent containing a succinic acid etc. on recorded media, the approach of recording in the ink containing an anion color is indicated by JP,64-9279,A.

[0008] Furthermore, the method of using the liquid constituent with which the method of giving the liquid constituent which makes JP,64-63185,A insolubilize a color to paper in advance of grant of ink contains in JP,8-224955,A the cationic matter with which molecular-weight-distribution fields differ with the ink containing an anionic compound is indicated, and the method of using the cationic matter and the liquid constituent containing a pulverizing cellulose for JP,8-72393,A with ink is indicated, respectively.

[0009] In these open official reports, image concentration is all high, printing grace and a water resisting property are good in them, and it is indicated that a good image is obtained also in color reproduction nature and bleeding. Furthermore, after recording in color ink on recorded media, the approach of giving the deck-watertight-luminaire-ized agent which forms a color and a lake is indicated by JP,55-150396,A, and giving the water resisting property of a record image is proposed.

[0010] How to mix ink and a particle content liquid constituent on recorded media : (3) To JP,4-259590,A After giving the colorless liquid containing the colorless particle which consists of mineral matter on recorded media, the approach to which nonaqueous recording ink is made to adhere is indicated. To JP,6-92010,A After giving the solution containing the solution containing a particle or a particle, and a binder polymer on recorded media, The approach to which the ink containing a pigment, water soluble resin, a water soluble solvent, and water is made to adhere is indicated. It is indicated that the record ingredient which contains in JP,2000-34432,A the liquid constituent which consists of a water-insoluble nature particle, and ink is indicated, and depend neither on a paper type, but printing grace and a color-enhancing good image are obtained.

[0011] Moreover, the solid ink injected and printed from a head by one side where it dissolved the color in the wax system constituent solidified in ordinary temperature as an approach of carrying out image formation to absorbency to a scarce base material conventionally and heating fusion is carried out is known. Furthermore, the thing using ultraviolet curing mold resin as the image formation approach to a plastic plate is indicated by JP,63-235382,A, JP,3-43292,A, JP,60-27589,B, JP,5-64667,B, JP,5-186725,A, JP,7-224241,A, JP,8-150707,A, JP,8-218018,A, etc.

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to this invention, absorbency scarce recorded media, such as a plastics metallurgy group, are also received especially. The color enhancement which was excellent in the coat paper average for ink jets, and the homogeneity of a color can obtain. There is little stripe nonuniformity of the solid image section, and the ink jet record image excellent also in the scratch-proof nature of a record image is obtained. And shelf life, the dependability in printing, the ink set that is excellent also in the dependability of specifically not producing the regurgitation stability or blinding from a recording head, the approach of forming the coloring section in recorded media, and an ink jet recording device are offered.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Thus, since the technical problem is left behind to the conventional approach by each, to much more high-definition ink jet record object, this invention persons came to have recognition that a new ink jet record technique needs to be developed in it rather than it asks in recent years. Based on the above-mentioned new knowledge, it succeeds in this invention. Namely, in order for this invention persons to adsorb or combine color material with this particle efficiently based on the above new knowledge, using the particle which has the operation which adsorbs color material By distributing this particle and using in the state of a liquid with ink, it becomes possible to make color material and a particle react by liquid-liquefied voice, and it came to succeed that the concentration and saturation of an image, weatherability, and scratch-proof nature can be raised with sufficient dependability as the result in a header and this invention.

[0020] Therefore, the purpose of this invention has the still larger color reproduction range. (The purpose of this invention) While offering the liquid constituent used in order to obtain the quality ink jet record object excellent also in the homogeneity of a color on absorbency scarce recorded media It excels in weatherability or scratch-proof nature, a record object is given, and it is in offering the dependability in printing, and the liquid constituent which is specifically excellent also in preservation stability and regurgitation stability from a recording head.

[0021] moreover, other purposes of this invention have the still larger color reproduction range, be excellent also in the homogeneity of a color, and they be in the point of offer the approach of form in recorded media the coloring section which be excellent also in the dependability in printing while there be still less stripe nonuniformity of the solid section and they can form the outstanding ink jet record object equipped also with good weatherability or scratch-proof nature on absorbency scarce recorded media.

[0022] Moreover, other purposes of this invention have the still wider color reproduction range, and it excels also in the homogeneity of a color. While generating of the stripe nonuniformity of the solid section can form the ink jet record object excellent also in the weatherability controlled by the good condition or scratch-proof nature on absorbency scarce recorded media It is in offering the ink set which combined the liquid constituent which is excellent also in the dependability in printing, and this liquid constituent, and an ink jet recording device.

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MEANS

[Means for Solving the Problem] Following this invention can attain the above-mentioned purpose. That is, this invention offers the ink set characterized by the anionic or cationic ink containing the solvent which dissolves color material, the polymerization nature component converted into a polymer by grant of energy, and this polymerization nature component, and the above-mentioned ink combining the liquid constituent which contains in reversed polarity the particle to which the front face is charged in the state of distribution.

[0024] Moreover, the above-mentioned ink set whose energy which gives this invention is ultraviolet rays, an electron ray, or heat; the above-mentioned ink set; particle which contains a photopolymerization initiator in a liquid constituent and/or ink further Preventing condensation of the color material in ink, in case the coloring section is formed on recorded media The above-mentioned ink set constituted so that this particle front face may be adsorbed in color material; a particle The above-mentioned ink set with which the color material in ink is constituted by the front face so that it may adsorb in the state of a single molecule in case the coloring section is formed on recorded media; ink Yellow ink, Magenta ink, cyanogen ink, black ink, The above-mentioned ink set which is at least one chosen from red ink, blue ink, and Green ink; ink The above-mentioned ink set which contains respectively yellow ink, Magenta ink, and cyanogen ink in the separate condition; ink offers the above-mentioned ink set which contains respectively yellow ink, Magenta ink, cyanogen ink, and black ink in the separate condition.

[0025] Moreover, the above-mentioned ink set which this invention has in the range whose ink is anionic and, whose F-potential of a liquid constituent is +5—+90mV; Ink is anionic. And the above-mentioned ink set whose primary dissociation constant electric dissociation exponent of an ink set; acid underwater [of the above by which pH of this liquid constituent is adjusted for the liquid constituent to 2-7 including the acid] is five or less; Ink has anionic. Ink And the above-mentioned ink set containing the pigment which has an anionic radical on a front face as the above-mentioned ink set; anionic compound which contains in ink the water soluble dye which has an anionic radical as the above-mentioned ink set; anionic compound which the anionic compound contains; A pigment, The above-mentioned ink set containing the anionic compound which is the dispersant of this pigment; Ink is cationicity. And the above-mentioned ink set in the range whose F-potential of a liquid constituent is -5—90mV; Ink is cationicity. And the above-mentioned ink set whose primary dissociation constant pKb of an ink set; base underwater [of the above by which pH of this liquid constituent is adjusted for the liquid constituent to the range of 7-12 including the base] is five or less; Ink has cationicity. And the above-mentioned ink set which the cationic compound contains in this ink; the above-mentioned ink set in the range whose mean particle diameter of a particle is 0.005-1 micrometer is offered.

[0026] Moreover, the process which gives the anionic or cationic ink containing the solvent which dissolves the polymerization nature component and this polymerization nature component which carry out the polymerization of this invention to (i) color material by grant of energy to recorded media, And it is the approach of forming the coloring section in the recorded media which have the process which gives the liquid constituent which contains in a polarity contrary to (ii) this ink the particle to which the front face is charged in the state of distribution to recorded media. The formation approach of the coloring section to the recorded media

characterized by being given so that the above-mentioned ink and a liquid constituent may touch the front face of the above-mentioned recorded media in the state of a liquid mutually is offered.

[0027] Moreover, the formation approach of the above-mentioned coloring section that a process (i) is performed after, as for this invention, a process (ii) is performed at least; after a process (i) is performed at least The formation approach of the above-mentioned coloring section that a process (ii) is performed; after a process (i) is performed The formation approach of the above-mentioned coloring section constituted so that a process (ii) may be performed and a process (i) may be performed again after that; the grant to the recorded media of the ink in a process (i) The formation approach of the above-mentioned coloring section performed by the ink jet record approach of a method of making this ink breathing out from an orifice according to a record signal; the ink jet record approach The formation approach of the above-mentioned coloring section which is the approach of making ink breathing out from an orifice by making heat energy acting on ink; the grant to the recorded media of the liquid constituent in a process (ii) The formation approach of the above-mentioned coloring section performed by the ink jet record approach of a method of making this liquid constituent breathing out from an orifice according to a record signal; the ink jet record approach After forming the coloring section by the approach more than formation approach; of the above-mentioned coloring section which is the approach of making heat energy acting on a liquid constituent, and making a liquid constituent breathing out from an orifice, The formation approach of the above-mentioned coloring section which performs the process which gives energy and carries out the polymerization of this polymerization nature component; the formation approach of the above-mentioned coloring section that the energy to give is ultraviolet rays, an electron ray, or heat is offered.

[0028] Moreover, the ink hold section which held the anionic or cationic ink containing the solvent which dissolves the polymerization nature component and this polymerization nature component which carry out the polymerization of this invention to color material by grant of energy, The 1st record unit equipped with the ink jet head for making this ink breathe out, The liquid constituent hold section which held the liquid constituent which contains in a polarity contrary to the above-mentioned ink the particle to which the front face is charged in the state of distribution, The ink jet recording device characterized by having the 2nd record unit equipped with the ink jet head for making this liquid constituent breathe out and the means which carries out the polymerization of this polymerization nature component is offered.

[0029] Moreover, the ink hold section which held the anionic or cationic ink containing the solvent in which this invention dissolves color material, the polymerization nature component converted into a polymer by grant of energy, and this polymerization nature component, The liquid constituent hold section which held the liquid constituent which contains in a polarity contrary to this ink the particle to which the front face is charged in the state of distribution, The ink jet head for making the ink held in the above-mentioned ink hold section, and the liquid constituent held in the above-mentioned liquid constituent hold section breathe out independently respectively, The ink jet recording apparatus characterized by having the means which carries out the polymerization of this polymerization nature component; an ink jet head The above-mentioned ink jet recording apparatus which is the thermal ink jet head which makes heat energy act and makes a liquid breathe out; the above-mentioned ink jet recording apparatus whose energy to give is ultraviolet rays, an electron ray, or heat is offered.

[0030] Moreover, this invention is given to recorded media with the anionic or cationic ink containing the solvent which dissolves the polymerization nature component and this polymerization nature component which carry out a polymerization to color material by grant of energy. It is a liquid constituent containing the particle used for forming the coloring section on these recorded media. The above-mentioned liquid constituent and the above-mentioned ink contact [formation of the above-mentioned coloring section] in the state of a liquid. And the liquid constituent characterized by being adsorbed, or joined together and made on it, the color material in ink holding an equivalent molecule condition substantially on the particle front face of a liquid constituent with the molecule condition which it has in ink is offered.

[0031]

[Embodiment of the Invention] Next, the gestalt of desirable operation is mentioned and this invention is explained in more detail. As a desirable embodiment of the approach of forming the coloring section in the recorded media of this invention (i) The process which gives the ink containing the color material of above-mentioned this invention etc. to recorded media, And it has the process which gives the liquid constituent of (ii) above-mentioned this invention to recorded media. And after constituting on the front face of the above-mentioned recorded media so that ink and a liquid constituent may touch in the state of a liquid mutually and it may be given, and forming the coloring section in it, the mode which gives energy and converts a polymerization nature component (a monomer may be called below) into a polymer is mentioned. By adopting this embodiment, it has a still larger color reproduction field, and excels also in the homogeneity of a color, and there is still less stripe nonuniformity of the solid section, and the ink jet record object equipped also with good weatherability or scratch-proof nature is stabilized on absorbency scarce recorded media, and it is obtained. Moreover, as the ink used for record and the liquid constituent itself were described above, since the configuration is very simple, the effectiveness that ink jet record of high quality and high-reliability can be performed is acquired. [0032] (Explanation of a mechanism) Although the reason outstanding effectiveness which was described above by this invention is done so is not clear, this invention persons think that it is based on the following reasons. First, the mechanism of the record in this invention is explained according to drawing 6 and drawing 7. In addition, the case where absorbency very scarce plastics is used for coincidence as recorded media as a liquid constituent using the water liquid constituent which contains the particle to which the front face is charged in cationicity in the state of distribution using the water color ink containing the polymerization nature component (monomer) converted into a polymer by the water soluble dye (anionic color) which has an anionic radical as ink, and energy grant is explained here.

[0033] Below, the record image concerning this invention is explained using drawing 6. First, language is defined in advance of explanation. Setting to this invention, the "single molecule condition" has pointed out that color material, such as a color and a pigment, is maintaining mostly the condition of having dissolved or distributed in ink. If it is the range to which saturation does not fall even if color material causes some condensation at this time, suppose that it is contained in this "single molecule condition." For example, since it is thought that it is desirable that it is a single molecule in the case of a color, suppose that it is called a "single molecule condition" also about color material other than a color for convenience. Moreover, in this invention, "the reaction of color material and a particle" shall mean the interaction of both ion-association besides both covalent bond, physical / chemical adsorption, absorption, adhesion, and others.

[0034] Drawing 6 is drawing having shown typically the condition that the coloring section I of the record image concerning this invention consisted of the main image section IM and its periphery IS. In drawing 6, the particle by which recorded media stick to 601 and color material 605 sticks to 603 chemically is shown typically. As shown in drawing 6, energy is given to the aggregate 607 and monomer of the particle 603 from which color material 605 stuck to homogeneity on the front face in the condition (it abbreviates to a "single molecule condition" henceforth) near a single molecule or a single molecule, and the particle holding the single molecule condition of color material, and the main image section IM is constituted from the ink jet record image of this invention by a polymerization and the three-dimensions crosslinked polymer 602 constructed for which the bridge and formed.

[0035] 609 is the aggregate of the particles which exist near the recorded-media front face in the main image section IM. The main image section IM is formed in a recorded-media front face of the process in which the process in which it adsorbs physically [a particle 603] or chemically, and color material 605 and a particle 603 adsorb by liquid-liquefied voice, and the process in which the whole coloring section I is stuck to solidification and recorded media by the three-dimensions crosslinked polymer which the monomer converted by energy grant. Therefore, the image formation excellent in weatherability or scratch-proof nature becomes it is rare to spoil the coloring property of the color material itself, and also in absorbency scarce record media, such as a plastics metallurgy group, image concentration and saturation are high, and the

color reproduction range is wide as much as coat paper, and possible. Since the color material 605 for which the particle front face 603 was not adsorbed but which remained into ink on the other hand is diffused in a longitudinal direction to recorded media 601, it forms a very small blot in Periphery IS by color material 605 and the three-dimensions crosslinked polymer 602 which the monomer converted. Thus, in order for color material to remain near the front face of a record medium 601 and to make a very small blot of ink form in a periphery, also in an image field with many amounts of ink grants, such as the shadow section and the solid section, white MOYA and color nonuniformity are excellent in the homogeneity of a color few.

[0036] Furthermore, when the liquid constituent of this invention is used, in case the particle aggregate 609 which exists near the front face of recorded media is formed, the pore of a certain amount of magnitude is formed in the interior of an aggregate. The color material 605 which existed independently in the above-mentioned ink can permeate the interior of pore of the particle aggregate 609, and it can stick to it in the state of a single molecule ideal for near an inlet port and the wall of pore, and it can make color material remain near the front face of recorded media in more ideal condition. The color-enhancing record object which was further excellent with this can be obtained.

[0037] Drawing 7 (1) - (5) is an outline process Fig. of the approach of forming the coloring section in the recorded media concerning this invention which explains like the outline sectional view and its formation fault of the coloring section [like] 700 1 operative condition. In drawing 7 , 701 is a part (it abbreviates to the "reaction section" henceforth) which mainly contains the reactant of ink and a liquid constituent, for example, the reactant of color material and a particle, and is a part equivalent to the main image section IM of drawing 6 . The ink which did not participate in a reaction with the particle in a liquid constituent substantially is the part (it abbreviates to the "ink outflow section" henceforth) formed by flowing into the verge of the reaction section 701, and 702 is equivalent to the periphery IS of drawing 6 R> 6. This coloring section 700 is the following, and is made and formed.

[0038] First, the color material 704 in ink and the liquid constituent 706 which has reactivity are given to recorded media 703 as a drop (drawing 7 (1)), consequently ***** 707 of a liquid constituent is formed (drawing 7 (2)). Within this ***** 707, it sticks to the particle 709 near the recorded-media front face physically on the surface of recorded media, or chemically. At this time, it is thought that there are some which a distributed condition becomes unstable and form the aggregate 711 of particles. On the other hand, in the part separated from the interface with the recorded media in ***** 707, it is thought that the particle 709 is maintaining the distributed condition of a basis.

[0039] Subsequently, ink 713 is given to recorded media 703 as a drop (drawing 7 (2)). Consequently, in the interface of ink 713 and ***** 707, color material 704 sticks to a particle 709 chemically first. Since this reaction is a reaction (liquid-liquid reaction) of liquid, color material 704 is in a single molecule condition, and it is thought that it sticks to homogeneity on the front face of a particle 709. That is, on a particle front face, even if color material does not cause condensation or they condense it, they are conjectured to be small. Consequently, many particles by which the surface section of the reaction section 701 was adsorbed in color material 704 in the state of the single molecule are formed, since color material can be made to remain in the state of a single molecule in the coloring section which affects coloring most, it is high image concentration and the high record image of saturation is formed.

[0040] Subsequently, it is thought that the particle to which these color material 704 stuck is condensed by particles since a distributed condition becomes unstable. That is, the aggregate 715 formed here holds the color material of a single molecule condition also to the interior. High image concentration and the record image of high saturation are formed of this aggregate 715.

[0041] Furthermore, a part of unreacted color material 704 diffuses the inside of ***** 707, and it sticks to the front face of the unreacted particle 709. Thus, since the reaction of color material and a particle advances further in the ***** 707 interior, an image with high saturation is formed more by high concentration. And since recorded media 703 are very deficient in absorbency, the contact probability of color material 704 and a particle 709 is raised, a reaction comparatively uniformly and fully advances, it is more uniform and the image excellent in the

concentration and saturation of an image is formed.

[0042] moreover — the time (drawing 7 (1)) of the liquid constituent 706 being given to recorded media 703, and the time of ink 713 being given to ***** 707 — (— when the dispersion medium which is distributing drawing 7 (2)) and a particle 709 changes, before distribution of a particle 709 becomes unstable and color material 704 adsorbs, what causes condensation between particles 709 exists. When change of a dispersion medium here points out physical-properties change of change generally observed, for example, pH of the liquid phase and solid content concentration, a solvent presentation, dissolved ion concentration, etc. when the liquid of a different kind beyond two sorts or it is mixed, and a liquid constituent contacts recorded media and ink, these change arises rapidly and complexly, destroys the distributed stability of a particle, and is considered to generate an aggregate.

[0043] It is surmised that these aggregates contribute to the further color-enhancing improvement by incorporating color material to the pore formed in the interior of the aggregate mentioned later. Moreover, although the aggregate formed within these ***** 707 has some which are sticking to recorded media, and what can move the inside of the liquid phase (it has a fluidity) exists, like the reaction process of the above-mentioned color material and a particle, color material stuck to the particle aggregate front face in the state of the single molecule, and formed the bigger aggregate on it, and this has also contributed what has a fluidity to color-enhancing improvement.

[0044] Moreover, in case the particle aggregate 711 which exists near the front face of the above-mentioned recorded media by using the liquid constituent of this invention is formed, the pore of a certain amount of magnitude is formed in the interior of an aggregate. The color material 704 which was not able to stick to the particle 709 in ***** 707 has some which permeate the interior of the particle aggregate 711 through pore with a solvent component. In that case, by sticking to near an inlet port and the pore wall of pore in a particle aggregate, more color material is efficient a front face and inside the particle aggregate 711, and color material 605 is adsorbed. Furthermore, since the pore diameter of the particle aggregate 711 is 1 to about several times the molecule size which exists in the ink of color material 704 when color material 704 is a color, condensation of color material cannot take place very easily, and the color material 704 which stuck to the interior of pore becomes possible [forming an ideal single molecule condition]. This can contribute to the further color-enhancing improvement greatly, and can obtain the record object which has the still larger color reproduction range.

[0045] Moreover, the pore physical properties of the particle aggregate 711 found out not only the particle contained in a liquid constituent but image formation being [in which it turns out that it is influenced with a solvent presentation etc., a particle aggregate is formed in from a liquid constituent, and the pore volume in a specific pore-radius field with this particle aggregate is formed on recorded media] ability, and that functionality was very high.

[0046] Furthermore, with the energy 716 from the outside, while carrying out a polymerization within [whole] the coloring section 700, it converts into the polymer which carried out three-dimensions bridge formation, and solidifies, and a monomer 705 sticks a monomer 705 to recorded media (drawing 7 (4)). In that case, in order to remove a solvent component beforehand, it can consider as the firm thing which hardened the coloring section 700 effectively by giving a desiccation process. According to this hardening process, recorded media 703 are pasted firmly and improvement in scratch-proof nature or weatherability of the coloring section 700 is attained.

[0047] In addition, although these have so far been explained by the case where it gives recorded media, in order of a liquid constituent and ink, if the liquid-liquid reaction of ink and a liquid constituent is attained, the order of grant to the recorded media of ink and a liquid constituent is not restricted to this at all, and it is ink first. Subsequently, you may be the order which gives a liquid constituent.

[0048] The liquid constituent and ink by which this invention is characterized below are explained to a detail. First, the definition of the cationic ink in this invention or anionic ink is described. Lessons is taken from the ion property of ink, and the electric charge of unacquainted ink itself is not carried out, but it being neutrality is setting to the technical field concerned and known in

itself. The component in ink, for example, color material, has an anionic radical or a cationic radical, and anionic ink here or cationic ink points out the ink currently adjusted so that these radicals may carry out behavior as an anionic radical or a cationic radical into ink. Moreover, the semantics is the same as that of the above also about an anionic or cationic liquid constituent. [0049] The liquid constituent of this invention is explained below to a <liquid constituent>.

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OPERATION

(Operation of a particle) When it mixes with adsorbing color material, without spoiling the color enhancement which color material originally has when it mixes with 1 ink, and 2 ink as an operation which the particle contained in a liquid constituent is expected in this invention, or when it is given to recorded media, distributed stability falling and remaining on the surface of recorded media etc. is mentioned. These operations may be attained by one sort or two sorts or more of particles.

[0050] It is mentioned that a particle presents ionicity contrary to color material as a property for fulfilling an operation of 1). Thereby, a particle can adsorb color material electrostatic. When color material is anionic, when color material is cationicity conversely, an anionic particle is used using a cationic particle. As an element which adsorbs color material in addition to ionicity, the configuration of the size, the mass, or the front face of a particle is mentioned. For example, the porosity particle which has much pores in a front face shows a characteristic adsorption property, and can adsorb color material in magnitude, a configuration, etc. of pore with two or more elements.

[0051] An operation of 2) is caused by the interaction with ink or recorded media. For this reason, although what is necessary is to just be attained by each configuration, presenting ionicity contrary to an ink presentation component or the constituent of recorded media as a property of a particle for example, is mentioned. Moreover, the distributed stability of a particle is influenced also by making an electrolyte live together in ink or a liquid constituent. In this invention, it is desirable to acquire one operation of the above 1 and the operations of two in an instant. Furthermore, it is desirable that an operation of the above 1 and 2 and both is acquired in an instant.

[0052] (Particle aggregate) Although a particle aggregate is formed near the front face of recorded media of the specific particle contained when the liquid constituent of this invention is used for image formation although the mechanism of record described previously, the pore of a certain amount of magnitude is formed in the interior of this aggregate. Then, the color material which existed independently in ink Since the interior of pore of this particle aggregate is permeated and near an inlet port and the wall of pore are adsorbed in the state of an ideal single molecule in case ink permeates the interior of recorded media, color material It will remain near the front face of recorded media more mostly, and it becomes possible to obtain the record object which has the color enhancement which was further excellent with this.

[0053] Therefore, as for the liquid constituent of this invention, it is desirable to constitute so that moderate pore may be formed in a particle aggregate in the case of image formation. Here, the pore formed of the particle contained in a liquid constituent can be measured by the following approach. That is, by the following approach, by measuring the pore volume in a certain specific pore-radius field, and constituting so that this value may become suitable within the limits, the mechanism of the above-mentioned record is performed and good image formation becomes possible about the particle aggregate obtained from the liquid constituent which contains a particle and a solvent at least. In measuring the physical properties of these particle aggregates, the liquid constituent which is the measuring object is first pretreated in the following procedures.

[0054] (1) Dry the liquid constituent which the particle contains at 120 degrees C under an atmospheric-air ambient atmosphere for 10 hours, make the amount of solvent evaporate mostly, and dry.

(2) Calcinate at 700 degrees C for 3 hours after carrying out the temperature up of the above-mentioned dry matter from 120 degrees C to 700 degrees C in 1 hour.

(3) Return the above-mentioned baking object to ordinary temperature gradually after baking, and fine-particles-ize a baking object.

The reason for performing the above-mentioned pretreatment here is for making a particle aggregate form from a liquid constituent by desiccation, removing the solvent component in a liquid constituent completely, emptying pore inside an aggregate, and forming an opening by baking.

[0055] In this invention, the nitrogen adsorption ****ing method can be suitably used as the pore radius of the pore of a particle aggregate, and a measuring method of pore volume. In this invention, when the size of the pore of the particle aggregate measured by such approach had the pore volume in the field whose pore radius is 3nm - 30nm in the specific range, it turned out that good image formation becomes possible. Although the reason nil why functionality is high is not clear, when the pore volume in the size field of this pore considers as range which described the pore radius above to guess to image formation ability Since it is easy to produce the color material inside a particle aggregate, and osmosis of a solvent component, it is thought that adsorption of the color material resulting from pore increases, and by suppressing light scattering of the pore itself that it is for the amount of color material which participates in substantial color-enhancing improvement to increase.

[0056] Therefore, it is effective as a measuring method of the color-enhancing ability of the formation image which measuring the pore volume in the field whose pore radius is 3nm - 30nm, and the field exceeding 30nm formed using the liquid constituent about the particle aggregate formed when the above pretreatments are performed to the liquid constituent of the measuring object. As a measuring method of the pore physical properties in this field, the approach by the nitrogen adsorption ****ing method is the most desirable. After a pore radius and pore volume carry out the vacuum deairing of the pretreated above-mentioned liquid constituent sample at 120 degrees C for 8 hours, it can ask for them from the nitrogen adsorption ****ing method from Barrett's and others approach (J. Am.Chem.Soc., Vol 73, 373, and 1951). Furthermore, a desirable measuring method is measuring the pore volume in the field whose pore radius's is 3nm - 20nm, and the field exceeding 20nm about the pore formed in the particle aggregate. In this range, since much more color-enhancing improvement is especially obtained when color material is a color, when measuring this color-enhancing ability, it is desirable.

[0057] (The pore radius and pore volume of a particle aggregate) The pore radius of a particle aggregate is considered that it is desirable that it is the range of 3nm - 30nm like the above-mentioned from a viewpoint which prevents the adsorption to prompt osmosis, near a pore inlet port, and the wall of color material, and condensation of the color material inside pore. Moreover, in order to incorporate only the color material which contributes to color-enhancing improvement inside, a certain amount of capacity is required for coincidence. Moreover, it is thought that the number of the pores in a particle aggregate also increases because pore volume increases, and it is thought that not only the amount of adsorption of the color material inside pore but the amount of adsorption near the inlet port of pore increases.

[0058] Therefore, the pore volume in the range whose pore radius is 3nm - 30nm is 0.4 or more ml/g, and the liquid constituent used suitable for this invention from these viewpoints has that desirable whose pore volume in the field in which a pore radius exceeds 30nm is 0.1ml/g or less, when the pore in a particle aggregate is measured by approach which was described above. In pore with a pore radius smaller than 3nm, neither color material nor a solvent component can permeate the interior of pore easily, and the pore of a particle aggregate does not contribute to color-enhancing improvement substantially. Moreover, since there is much pore with big light scattering when pore volume exceeds 0.1 ml/g in the field to which a pore radius exceeds 30nm, it is hard coming to contribute the color material which stuck near a pore inlet port and to a wall to color enhancement. Moreover, since there are few the color material and the solvent

components which permeate the interior of a particle aggregate when the pore volume in the field of the above-mentioned pore radius is under this range, the amount of color material which sticks to near an inlet port and the interior of pore decreases and the contribution to color-enhancing improvement becomes low, it is not desirable.

[0059] As more desirable range, the pore volume in the range whose pore radius is 3nm - 20nm is 0.4 or more ml/g, and it is desirable to use that whose pore volume in the field in which a pore radius exceeds 20nm is 0.1 or less ml/g. When the pore of the range of a radius whose pore is 3nm - 20nm exists mostly, and a color is especially used for color material, color enhancement improves further and can form the image which has the still larger color reproduction range. The pore radius and pore volume of the particle aggregate formed from a liquid constituent change with the chemical species of the particle contained, a configuration and not only magnitude but a solvent kind, other additives, those presentation ratios, etc., and are considered that the formation condition of a particle aggregate is controllable by controlling these conditions. Therefore, when producing the liquid constituent of this invention, it is desirable to take these things into consideration and to make it the configuration of the pore formed in a particle aggregate become within the limits of the above.

[0060] Next, the liquid constituent containing cationicity or an anionic particle is explained concretely.

[Cationic liquid constituent] As a cationic liquid constituent, the liquid constituent with which stability comes to distribute this particle is mentioned, for example including the particle which has a cationic radical on a front face. In this invention, the thing by which pH was adjusted to 2-7 as a cationic liquid constituent including the acid, and the thing whose F-potential is +5-+90mV can be used suitably.

[0061] (pH and F-potential) The F-potential of a liquid constituent is described. The basic principle of F-potential is shown below. Generally, when an isolation charge is on the surface of solid phase in the system which the solid-state is distributing in a liquid, it appears so that the electric charge layer of an opposite charge may maintain electrical neutrality at the liquid phase near a solid phase interface. This is called an electric dipole layer and is calling F-potential the thing of the potential difference by this electric dipole layer. When F-potential is plus, the front face of a particle shows cationicity and shows anionic by minus. Generally, the electrostatic repulsive force committed between particles becomes strong, dispersibility is said to be good, and it is possible that the ionicity on the front face of a particle is strong to coincidence, so that the absolute value is high. That is, it can be said that cationicity is so strong that the F-potential of a cationic particle is high, and the force which draws the anionic compound in ink is strong.

[0062] When the liquid constituent which is in the range whose F-potential is +5-+90mV as a result of this invention persons' inquiring wholeheartedly was used, the coloring section which it comes to form on recorded media found out presenting the especially excellent coloring property. Although the reason is not certain, since the cationicity of a particle is moderate and an anionic compound probably sticks to homogeneity thinly on a particle front face, without condensation of a rapid anionic compound (anionic color material) taking place, it is thought that it is hard to form a lake with a huge color material, consequently the coloring property of color-material original is discovered in the better condition. Furthermore, with the cationic liquid constituent of this invention, even after adsorbing an anionic compound on a particle front face, while a particle condenses a particle presenting weak cationicity because it will be in a distributed unstable state, it adsorbs easily on the surface of recorded media, and it is thought that it is easy to remain near the front face of recorded media.

[0063] Consequently, it is thought that the next outstanding effectiveness is acquired. That is, in an image field with many the coloring property which was excellent in the coat paper average for ink jets also to media, such as not only a regular paper but an absorbency scarce plastics metallurgy group, and the amounts of ink grants, such as the shadow section and the solid section, there are little white MOYA and color nonuniformity and they become the thing excellent in the homogeneity of a color. Moreover, since the amount of grants of a cationic particle can also be lessened in order that an anionic compound may adsorb and color to a particle very efficiently compared with coat paper, when it especially prints in a regular paper,

aesthetic property of paper is not spoiled and it excels also in the scratch-proof nature of a record image. When F-potential uses the liquid constituent containing the cationic particle in the range which is +10—+85mV as range of more desirable F-potential, for example When solid printing is carried out, the boundary between dots stops being able to be conspicuous easily, and much more reduction of stripe nonuniformity with a head scan can be attained. Further If F-potential uses the liquid constituent containing a cationic particle in the range which is +15—+65mV, it will not be based on a medium kind but it will become possible to obtain the image which has the extremely excellent color enhancement.

[0064] As for pH of the cationic liquid constituent of this invention, it is desirable that it is in the range of 2—7 near 25 degree C from an adsorbent viewpoint of preservation stability and an anionic compound. Since the stability of an anionic compound is not remarkably reduced when a liquid constituent is mixed with anionic ink within the limits of this pH, strong condensation of anionic compounds is not caused, and the saturation of a record image can fall or it can prevent becoming the somber image effectively. Moreover, since the distributed condition of a cationic particle is also good in above-mentioned it being within the limits, the preservation stability of a liquid constituent and the regurgitation stability from a recording head are maintainable good. Furthermore, when it mixes with ink, since a cationic particle front face is fully adsorbed, the anionic matter can obtain the outstanding color-enhancing ink jet record object. As range of more desirable pH, pH is 3—6, and in this range, while being able to prevent the corrosion of the recording head by the mothball very effectively, it improves one layer of scratch-proof nature nearby of a record image.

[0065] (Cationic particle) Next, the component which constitutes the cationic liquid constituent of this invention is described. The cationic particle mentioned as the 1st component requires that the front face of the particle itself presents cationicity in the condition of having distributed in the liquid constituent, in order to attain the above-mentioned operation effectiveness. When it mixes with anionic ink by making a front face into cationicity, an anionic color material sticks to a particle front face promptly, and the ink jet record object of sufficient image concentration is obtained by leaving color material to homogeneity on a recorded-media front face in the state of a single molecule. On the other hand, a particle front face is not cationicity, and when the particle and the water-soluble cationic compound exist separately in a liquid constituent, in order that color material may spoil the coloring property of a lifting and the color material itself for condensation centering on a cationic compound, it becomes difficult to attain the color enhancement of the coat paper average for ink jets. Therefore, although the front face needs to be cationicity, if the particle used for the liquid constituent of this invention is a particle by which the front face was cation-ized by processing even if it is a particle which is originally anionic or neutrality electrostatic not to mention the particle which is essentially cationicity, it can be used for the liquid constituent of this invention.

[0066] If pore is formed in the aggregate by these particles formed on recorded media, the cationic particle suitably used by this invention will come out enough for attaining the purpose of this invention, and, for a certain reason, will not be especially limited to the ingredient kind of a particle. As an example, the silica and alumina which were cation-ized, hydrated alumina, a titania, a zirconia, boria, silica boria, Seria, a magnesia, a silica magnesia, a calcium carbonate, a magnesium carbonate, a zinc oxide, hydrotalcites, etc. these compound particles, an organic particle, an inorganic organic compound particle, etc. are mentioned, for example. These cationic particles can mix and use one sort or two sorts or more.

[0067] Since the particle front face has positive charge when hydrated alumina is used especially as a particle, it is desirable, and it is desirable in respect of the color enhancement excellent in the hydrated alumina which is an X-ray diffraction method and shows **—dynamite structure especially, the homogeneity of a color, preservation stability, etc. Hydrated alumina is defined by the following general formula.

aluminum₂O — the inside of $3-n(\text{OH})_2n$ and, and the $m\text{H}_2\text{O}$ above-mentioned type, and n — one of the integers of 0—3 — expressing — m — 0—10 — it has the value of 0—5 preferably. In many cases, the expression of $m\text{H}_2\text{O}$ cannot express the aqueous phase which does not participate in formation of a crystal lattice and which can be ****ed, and the value whose m is

not an integer can also be taken. However, in m and n , 0 does not become coincidence.

[0068] The (020) field is the stratified compound which forms a huge flat surface, and the crystal of hydrated alumina in which boehmite structure is generally shown shows a diffraction peak peculiar to an X-ray diffraction pattern. The structure which is called the pseudo-boehmite other than perfect boehmite and which contained superfluous water between the layers of a field (020) can also be taken. The X-ray diffraction pattern of this pseudo-boehmite shows a diffraction peak [broadcloth / boehmite].

[0069] Since distinction of boehmite and pseudo-boehmite is clearly impossible, unless it refuses, especially by this invention, it is called the hydrated alumina (henceforth hydrated alumina) which shows boehmite structures including both. (020) a field — a spacing — crystal thickness measures the peak to which diffraction rate 2θ appears in 14–15 degrees, whenever [angle-of-diffraction / of a peak], from 2θ and half-value width B , a spacing is Bragg's (Bragg) formula and (020) can ask for crystal thickness using the formula of SHIERA (Scherrer). (020) The spacing of a field can be used as the hydrophilic property and the hydrophobic standard of hydrated alumina. Although not limited, if it is the approach that hydrated alumina with boehmite structure can be manufactured, especially as the manufacture approach of hydrated alumina used by this invention, it can manufacture by well-known approaches, such as hydrolysis of an aluminum alkoxide, and hydrolysis of a sodium aluminate, for example.

[0070] The hydrated alumina of amorphism can be changed and used for boehmite structure by heat-treating above 50 degrees C under existence of water in X diffraction as indicated by JP,56-120508,A. Especially the approach of using preferably is an approach of obtaining hydrated alumina, by adding an acid to a long-chain aluminum alkoxide, and performing hydrolysis and amalgam decomposition. Here, carbon numbers are five or more alkoxides, and when the alkoxide of carbon numbers 12–22 is used further, since removal of the alcohol content in a manufacture process and configuration control of hydrated alumina become easy so that it may mention later, it is desirable [a long-chain aluminum alkoxide].

[0071] as the acid to add — one sort out of an organic acid and an inorganic acid — or although two or more sorts can be chosen freely and can be used, a nitric acid is the most desirable in respect of the reaction effectiveness of hydrolysis and the obtained configuration control of hydrated alumina, or dispersibility. It is also possible to perform hydrothermal synthesis etc. after this process and to control particle diameter. If hydrothermal synthesis is performed using the dispersion liquid of the hydrated alumina containing a nitric acid, the nitric acid in a water solution is incorporated as a nitric-acid root on a hydrated alumina front face, and it can raise water-dispersion [of this hydrate]. Moreover, after hydrothermal synthesis, an acid can be suitably added to a hydrated alumina slurry, and the hydrated alumina slurry of very stable high solid content concentration can be prepared by little acid concentration by adjusting and condensing pH. When such a slurry is used, the liquid constituent which did not need to ** separately the acid mentioned later outside and was excellent in the distributed stability of a hydrated alumina particle can be produced.

[0072] The approach by hydrolysis of the above-mentioned aluminum alkoxide has the advantage of being hard to mix impurities, such as various ion, as compared with the approach of manufacturing an alumina hydrogel and a cationic alumina. Furthermore, as for a long-chain aluminum alkoxide, the long-chain alcohol after hydrolysis also has the advantage that dealcoholization of hydrated alumina can be performed completely, as compared with the case where the alkoxide of short chains, such as aluminiumisopropoxide, is used. As for pH of the solution at the time of initiation of hydrolysis, setting less than to six is desirable. Since the hydrated alumina finally obtained will become a crystalline substance if pH exceeds 8, it is not desirable.

[0073] Moreover, as hydrated alumina used by this invention, if boehmite structure is shown with an X-ray diffraction method, the hydrated alumina containing metallic oxides, such as a titanium dioxide, can also be used. Since optical density becomes high, 0.01 – 1.00 mass % of hydrated alumina is desirable, and it is 0.13 to 1.00 mass % more preferably, the rate of adsorption of color material becomes quick, and a blot and beading stop easily being able to generate the content

ratio of metallic oxides, such as a titanium dioxide. Furthermore, said titanium dioxide requires that the valence of titanium should be + tetravalence. The content of a titanium dioxide can be dissolved to boric acid, and can be investigated by the ICP method. Moreover, distribution of the titanium dioxide in hydrated alumina and the valence of titanium can be analyzed using ESCA. [0074] It can reach for 100 seconds with argon ion, the front face of hydrated alumina can be etched for 500 seconds, and change of the content of titanium can be investigated. If the valence of titanium becomes smaller than + tetravalence, a titanium dioxide will come to commit a titanium dioxide as a catalyst, the weatherability of a record image falls or yellowing of a record image becomes easy to take place.

[0075] content of a titanium dioxide — the near front face of hydrated alumina — although it is good, you may contain to the interior. Moreover, a content may be missing from the interior and may be changing from the front face. If the titanium dioxide contains only very near the front face, since the electrical characteristics of hydrated alumina will be easy to be maintained, it is still more desirable.

[0076] as the manufacture approach of the hydrated alumina containing a titanium dioxide — ***** "surface science" — the method of hydrolyzing and manufacturing the mixed liquor of an aluminum alkoxide which is indicated by the 327th page (the volume for Kenji Tamaru, 1985), and a titanium alkoxide is desirable. When hydrolyzing the mixed liquor of said aluminum alkoxide and titanium alkoxide as the other approaches, hydrated alumina can also be added and manufactured as a nucleus of crystal growth.

[0077] Instead of a titanium dioxide, oxides, such as a silica, magnesium, calcium, strontium, barium, zinc, boron, germanium, tin, lead, a zirconium, an indium, phosphorus, vanadium, niobium, a tantalum, chromium, molybdenum, a tungsten, manganese, iron, cobalt, nickel, and a ruthenium, are made to contain, and can be used. For example, the hydrated alumina containing a silica has effectiveness in improvement in the scratch-proof nature of a record image.

[0078] The liquid constituent which the hydrated alumina used suitable for this invention was the thing of the range whose spacing of that (020) field is 0.614–0.626nm, and whose distributed stability of the hydrated alumina particle in the inside of a liquid constituent was good within the limits of this, and was excellent in preservation stability or regurgitation stability is obtained. Although this reason is not certain, if [above-mentioned] the spacing of a field (020) is within the limits, since it is the range where both the ratios of the hydrophobicity of hydrated alumina and a hydrophilic property are moderate, that to which the regurgitation stability of a liquid constituent becomes good is conjectured in a liquid constituent according to distributed being stability by moderate repulsion of particles, or the wettability balance inside a delivery being moderate.

[0079] Moreover, the range of hydrated alumina whose crystal thickness of that (020) field is 4.0–10.0nm is desirable, and since transparency and adsorbent [of color material] are excellent in it being this within the limits, it is desirable. Since correlation has the crystal thickness of the spacing of a field (020), and a field (020) according to this invention persons' knowledge, if the spacing of a field (020) is above-mentioned within the limits (020), the crystal thickness of a field can be adjusted to the range of 4.0–10.0nm.

[0080] Furthermore, since the alumina (aluminum oxide) generated by heat treatment of calcining (calcination) etc. in the above-mentioned hydrated alumina, metal aluminum, or an aluminum salt has positive charge similarly, it is used suitably. As an alumina, there are alpha mold, gamma mold, and a thing that has the crystallized state of delta, chi, eta, rho, beta mold, etc. further, it is the form where the front face was maintained at cationicity, and all can be used if it distributes stably underwater. Especially, a front face is activity, gamma mold has the high adsorption power of color material, since it also tends to form the stable particle dispersing element atomized comparatively, is excellent in color enhancement, shelf life, regurgitation stability, etc., and can be used suitably.

[0081] Moreover, as for a cationic particle which is used by this invention and which was described above, the thing of the range whose mean particle diameter measured by the dynamic-light-scattering method is 0.005–1 micrometer is suitably used from viewpoints, such as color enhancement after printing, the homogeneity of a color, and preservation stability. Within the

limits of this, too much osmosis can be effectively prevented inside absorbency high recorded media like a regular paper, and the homogeneous fall of color enhancement or a color can be suppressed. Moreover, it is also suppressed that a cationic particle sediments in a liquid constituent, and it can also prevent the fall of the preservation stability of a liquid constituent effectively. More preferably, mean particle diameter is a thing within the limits which are 0.01–0.8 micrometers, and if such a particle is used, the texture of the scratch-proof nature of the image after printing to recorded media, or a record object will become desirable especially. Furthermore, mean particle diameter is a thing within the limits which are 0.03–0.3 micrometers, and since the pore of the particle aggregate formed on recorded media is easy to be formed effectively in the pore-radius field made into the purpose, such a particle has it. [preferably desirable]

[0082] (The pore physical properties and configuration of a cationic particle) It makes color material stick to the front face of the particle itself efficiently, and also the maximum pore radius of the particle in the nitrogen adsorption ****ing method is 2–12nm, and that whose total pore volume is 0.3 or more ml/g is desirable [a particle] again at the same time a cationic particle which is used by this invention and which was described above forms efficiently the pore of the particle aggregate formed on recorded media. The maximum pore radius of a particle is 3m – 10nm more preferably, and since the pore of the particle aggregate formed on recorded media is easy to be formed effectively in the pore-radius field made into the purpose, that whose total pore volume is 0.3 or more ml/g is desirable.

[0083] When the adsorption site of the color material on the front face of a particle exists enough that it is within the limits the BET specific surface area of whose is 70–300m²/g, the above-mentioned particle used by this invention becomes easy to leave color material near the front face of recorded media in the state of a single molecule more effectively, and contributes to color-enhancing improvement.

[0084] Moreover, the configuration of the particle used by this invention can make ion exchange water able to distribute a particle, can be dropped on a collodion membrane, can produce a test sample, and can observe and ask for it with a transmission electron microscope. In case a particle aggregate is made to form on recorded media in this invention, it is the point of making pore forming in an aggregate, and the non-globular form thing in which the particle configuration forms the aggregated particle which the shape of a needle, the monotonous configuration, or the spherical primary particle had a certain directivity, and was connected, such as the shape of the shape of a rod or a necklace, can be used suitably.

[0085] According to this invention persons' knowledge, plate-like one of the dispersibility to water is better than the shape of a needle, and a pilliform bundle (cilia **), and since the orientation of a particle becomes random when a particle aggregate is formed and pore volume becomes large, the configuration of a particle is more desirable. A pilliform bundle configuration means the condition that the needlelike particle touched in side faces and gathered like the bundle of the hair of hair here. it is indicated by reference (Rocek J., etal, Applied Catalysis, 74 volumes, 29–36 pages, 1991) at pseudo-boehmite also in the hydrated alumina which can be preferably used especially by this invention — as — cilia — generally it is known that there are a ** and the other configuration.

[0086] It can ask for the aspect ratio of the particle of a monotonous configuration by the approach defined as JP,5-16015,B. An aspect ratio is shown by the ratio of a diameter to the thickness of a particle. The diameter of circle which has an area equal to the projected area of the particle when observing hydrated alumina with a microscope or an electron microscope shall be indicated to be a diameter here. An aspect ratio is expressed in the ratio of the diameter which observes similarly and shows the minimum value of a monotonous side, and the diameter which shows maximum as an aspect ratio. Moreover, in the case of a pilliform bundle configuration, the method of asking for an aspect ratio can find an up-and-down diameter of circle and die length, respectively by the ability using as a cylinder each needlelike hydrated alumina particle which forms a pilliform bundle, and can take and ask it for the ratio. the configuration of the most desirable hydrated alumina — plate-like — an average aspect ratio — the range of 3–10 — moreover, by the pilliform bundle, the range of 3–10 has a desirable average

aspect ratio. Since a clearance is easy to be formed between particles when the average aspect ratio was within the limits and it forms [above-mentioned] a particle aggregate, a vesicular structure can be formed easily.

[0087] The content of a cationic particle in the liquid constituent of this invention which was described above is the range suitable although what is necessary is just to determine the optimal range suitably, when the range of 0.1 – 40 mass % attains the purpose of this invention according to the class of matter to be used, and the range of one to 30 mass %, and further 3 – 15 mass % is more preferably suitable for it. At such within the limits, the image of coloring which depended and was excellent in the medium kind can be obtained to stability, and it excels also especially in the preservation stability and regurgitation stability of a liquid constituent.

[0088] (Acid) As stated previously, as for the liquid constituent of this invention, it is desirable that pH is adjusted to 2–7 including an acid. While an acid raises the distributed stability of the particle in the inside of liquid by ionizing a cationic particle front face and raising surface potential, the role of the adsorption disposition top of the anionic compound in ink (anionic color material) and the viscosity control of a liquid constituent is played. Combining the cationic particle to be used, the acid used suitable for this invention will not be limited, especially if physical properties, such as desired pH, and F-potential or particle dispersibility, are acquired, but it can be used, choosing it to the next inorganic acid, the next organic acid, etc. freely.

[0089] As an inorganic acid, a hydrochloric acid, a sulfuric acid, a sulfurous acid, a nitric acid, a nitrous acid, phosphoric acid, boric acid, carbonic acid, etc. are mentioned, and, specifically, a carboxylic acid which is listed below, a sulfonic acid, amino acid, etc. are mentioned as an organic acid, for example.

[0090] As a carboxylic acid, for example A formic acid, an acetic acid, a chloroacetic acid, dichloroacetic acid, A trichloroacetic acid, gibblar poison, trimethylacetic acid, a methoxy acetic acid, mercaptoacetic acid, A glycolic acid, a propionic acid, butanoic acid, a valeric acid, a caproic acid, a caprylic acid, A capric acid, a lauric acid, a myristic acid, a palmitic acid, stearin acid, Oleic acid, linolic acid, a linolenic acid, cyclohexane carboxylic acid, A phenylacetic acid, a benzoic acid, ortho toluylic acid, meta toluylic acid, para toluylic acid, O-chlorobenzoic acid, m-chloro benzoic acid, para chlorobenzoic acid, o-BUROMO benzoic acid, m-BUROMO benzoic acid, p-BUROMO benzoic acid, o-nitro benzoic acid, m-nitro benzoic acid, P-nitrobenzoic acid, oxalic acid, a malonic acid, a succinic acid, a glutaric acid, An adipic acid, a tartaric acid, a maleic acid, a fumaric acid, a citric acid, a phthalic acid, Isophthalic acid, a terephthalic acid, a salicylic acid, para hydroxybenzoic acid, an anthranilic acid, m-aminobenzoic acid, p-aminobenzoic acid, o-methoxy benzoic acid, m-methoxy benzoic acid, para methoxy benzoic acid, etc. are mentioned.

[0091] Moreover, as a sulfonic acid, benzenesulfonic acid, a methylbenzene sulfonic acid, an ethylbenzene sulfonic acid, dodecylbenzenesulfonic acid, 2 and 4, 6-trimethyl benzenesulfonic acid, 2, 4-dimethylbenzene sulfonic acid, 5-sulfosalicylic acid, 1-sulfo naphthalene, 2-sulfo naphthalene, a hexane sulfonic acid, an octane sulfonic acid, a dodecane sulfonic acid, etc. are mentioned, for example.

[0092] Moreover, as amino acid, a glycine, an alanine, a valine, alpha-aminobutyric acid, gamma-aminobutyric acid, the beta-alanine, a taurine, a serine, epsilon-amino-n-caproic acid, a leucine, a norleucine, a phenylalanine, etc. are mentioned.

[0093] and the liquid constituent of this invention — setting — these acids — one sort — or two or more sorts can use it, mixing. Also in these acids, since it excels in the distributed stability of a cationic particle, or adsorbent [of an anionic compound], the underwater primary dissociation constant pka can use especially five or less thing suitably. Specifically as such an acid, a hydrochloric acid, a nitric acid, a sulfuric acid, phosphoric acid, an acetic acid, a formic acid, oxalic acid, a lactic acid, a citric acid, a maleic acid, a malonic acid, etc. are mentioned.

[0094] It is desirable when making it A:B=200:1–5:1 and become the range of 150:1–8:1 more preferably aims at improvement in the distributed stability of a cationic particle, and adsorbent improvement to the particle front face of an anionic compound for the mixed ratio of a cationic particle (A) and an acid (B) in a liquid constituent on mass criteria in the liquid constituent of this invention.

[0095] (Other constituents) Next, the component of others which constitute a cationic liquid constituent is explained concretely. Although the cationic liquid constituent of this invention usually contains water as a solvent object, including the above-mentioned cationic particle, an acid, a photopolymerization initiator which was preferably described above, etc., its thing containing the organic solvent for dissolving the further below-mentioned monomer and other additives is desirable.

[0096] As an organic solvent to be used, for example In this case, dimethylformamide, amides [, such as dimethylacetamide,]: — ketones [, such as an acetone,]: — a tetrahydrofuran — Polyalkylene glycols, such as ether, such as dioxane, a polyethylene glycol, and a polypropylene glycol : Ethylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, Alkylene glycol, such as a diethylene glycol : Ethylene glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol monomethyl ether and the triethylene glycol monomethyl ether : Ethanol, [others / monohydric alcohol, such as isopropyl alcohol, n-butyl alcohol, and isobutyl alcohol,] A glycerol, a N-methyl-2-pyrrolidone, 1, 3-dimethyl-imidazolidinone, Aliphatic hydrocarbon, such as aromatic-hydrocarbon:hexanes, such as benzene, such as triethanolamine, a sulfolane, and dimethyl sulfoxide, toluene, and a xylene, an octane, and a heptane, Propylene carbonate etc. is mentioned. Although there is especially no limit about the content of the above-mentioned organic solvent, further 5 - 60% is the suitable range 5 to 90% of liquid constituent all mass, for example.

[0097] Moreover, additives, such as a viscosity controlling agent, pH regulator, antiseptics, various surface active agents, an anti-oxidant and an evaporation accelerator, a water-soluble cationic compound, and binder resin, may be further blended with the liquid constituent of this invention suitably if needed. Especially selection of a surfactant is important, when [to the recorded media of a liquid constituent] getting wet and adjusting *****. For the purpose of control of the bleeding in unique image fields, such as the further cationic grant of a liquid constituent, improvement in alphabetic character grace, etc., in the range which does not check the operation effectiveness of this invention, a water-soluble cationic compound is chosen freely and can be added.

[0098] As a water-soluble cationic compound, specifically For example, the poly allylamine, a polyamine sulfone, a polyvinyl amine, The neutralization object or partial neutralization objects by the acid, such as chitosan and these hydrochloric acids, or an acetic acid, The compound which cation-ized some Nonion nature compounds of a giant molecule For example, the copolymer of vinyl pyrrolidone and the 4th class salt of an amino alkyl alkylate, It can be used from a copolymer, etc. a compound of the 1st class, the 2nd class, and a tertiary amine salt type, such as a cationic surfactant, in addition to this, an amino acid mold amphoteric compound, etc. of acrylamide and the 4th class salt of aminomethyl acrylamide, being able to choose one sort or two sorts or more.

[0099] Binder resin is the purposes, such as improvement in the further scratch-proof nature of a cationic particle, it can be used together in the range which does not spoil the preservation stability or regurgitation stability of the texture of recorded media, or a liquid constituent, for example, can be freely chosen to a water-soluble polymer, a polymer emulsion, polymeric latex, etc., and can be used. Moreover, as mentioned later, it is a desirable gestalt in the preservation stability of a liquid constituent and ink to add a photopolymerization initiator and a sensitizer in a liquid constituent at the same time it promotes efficiently hardening (a monomer should carry out a polymerization and a generation polymer object should construct a bridge by grant of energy) of a monomer.

[0100] (Surface tension of a liquid constituent) The liquid constituent of this invention may be toned according to the color of recorded media, although colorlessness or a white thing is more desirable. Furthermore, as suitable range of the various physical properties of the above liquid constituents, surface tension is more preferably made into 10 - 40 mN/m (dyn/cm) ten to 60 mN/m (dyn/cm), and viscosity is made into 1 - 30 mPa·s (cP).

[0101] Although the anionic liquid constituent of [anionic liquid constituent] this invention makes an indispensable constituent the particle which has an anionic radical on a front face and is characterized by this particle distributing to stability, that by which pH is further adjusted to 7-

12 including the base, and its thing whose F-potential is $-5-90\text{mV}$ are desirable.

[0102] (pH and F-potential) As a result of this invention persons' inquiring wholeheartedly, it found out that the anionic liquid constituent in the range whose F-potential is $-5-90\text{mV}$ presented the coloring property in which the front face of an anionic particle was especially adsorbed especially efficiently, and the cationic compound in ink (cationic color material) was excellent on recorded media. Although the reason is not certain, as well as the case of the cationic liquid constituent probably explained previously since anionic [of a particle] is moderate, color material does not form a huge lake in a particle front face by sticking to homogeneity thinly, without rapid condensation of the cationic compound in ink taking place, but it is thought that the coloring property of color-material original is discovered better.

Furthermore, in the anionic liquid constituent of this invention, after adsorbing a cationic compound on a particle front face, it becomes distributed instability, and it is thought that particles condense by the concentration change at the time of a solvent component evaporating and permeating on recorded media, and it becomes easy to remain near the front face.

[0103] Consequently, it is thought that the next outstanding effectiveness is acquired. That is, in an image field with many amounts of ink grants, such as the coloring property and the shadow section which were excellent in the coat paper average for ink jets, and the solid section, white MOYA and color nonuniformity are excellent in the homogeneity of a color few. Moreover, in order for a cationic compound to stick to a particle front face and to color on it very efficiently compared with coat paper, when the amount of grants of an anionic particle can also be lessened and is especially printed in a regular paper, the aesthetic property of paper is maintained, and the scratch-proof nature of a record image also becomes good. The range of the range of more desirable F-potential is $-10-85\text{mV}$, when the liquid constituent containing the anionic particle which has the F-potential of such range is used, and it carries out solid printing, the boundary between dots stops being able to be conspicuous easily, and it can attain much more reduction of stripe nonuniformity with a head scan. Furthermore, if F-potential uses preferably the liquid constituent containing the anionic particle in the range which is $-15-65\text{mV}$, it will not be based on a recorded-media kind, but it will become possible to obtain the image which has the extremely excellent color enhancement.

[0104] As for pH of the anionic liquid constituent of this invention, it is desirable that it is the range of 7-12 near [an adsorbent viewpoint to] 25 degree C of the cationic compound in preservation stability and ink. Since the stability of a cationic compound (color material) is not remarkably reduced when it mixes with cationic ink to this pH within the limits, strong condensation of cationic compounds is not caused, and the saturation of a record image can fall or it can prevent becoming the somber image effectively. Moreover, if there is pH within above limits, since the dispersibility of an anionic particle is also good, the preservation stability of a liquid constituent and the regurgitation stability from a recording head are maintainable good. Furthermore, when it mixes with ink, the color-enhancing ink jet record object in which the anionic particle front face was fully adsorbed, and the cationic matter was excellent is obtained. The range of pH of a more desirable liquid constituent is 8-11, and it improves one layer of scratch-proof nature nearby of a record image while it can prevent the corrosion of the recording head by the mothball very effectively, if pH is this within the limits.

[0105] (Anionic particle) Next, the component which constitutes the anionic liquid constituent of this invention is described. In order to attain the above-mentioned operation effectiveness, as for the anionic particle mentioned as 1st indispensable component, it is desirable that it is what the front face of the particle itself presents anionic in the condition of having distributed in the liquid constituent. When it mixes with cationic ink by making a particle front face anionic, a cationic color material can be adsorbed on a particle front face, and the ink jet record object of sufficient image concentration is obtained by leaving color material to homogeneity on a recorded-media front face in the state of a single molecule.

[0106] On the other hand, a particle front face is not anionic, and when the particle and the water-soluble anionic compound exist separately in a liquid constituent, in order that color material may spoil the coloring property of a lifting and the color material itself for condensation centering on an anionic compound, it becomes difficult to attain the color enhancement of the

coat paper average for ink jets. Therefore, although it is required to have charged the front face in anionic, the particle used with the liquid constituent of this invention can be used if it is the particle by which the front face was anion-ized by processing, even if it is originally a cationic or neutral particle electrostatic not to mention the particle which is essentially anionic.

[0107] The anionic particle suitably used by this invention is enough to attain the purpose of this invention if pore is formed in the aggregate by these particles formed on recorded media, and especially the ingredient kind of a particle is not limited. As an example, the silica and titania which were anion-ized, a zirconia, boria, silica boria, Seria, a magnesia, a silica magnesia, a calcium carbonate, a magnesium carbonate, zinc oxides, etc. these compound particles, an organic particle, an inorganic organic compound particle, etc. are mentioned, for example. and the liquid constituent of this invention — setting — these — one sort — or two or more sorts can use it, mixing.

[0108] Moreover, the thing of the range whose mean particle diameter measured by the dynamic-light-scattering method from a viewpoint of the color enhancement of the ink after printing, the homogeneity of a color, and preservation stability is 0.005–1 micrometer is suitable for the anionic particle used by this invention like the case of the cationic particle explained previously. More preferably, mean particle diameter is a thing within the limits which are 0.01–0.8 micrometers, and if such a particle is used, scratch-proof nature and texture after printing to recorded media will become desirable especially. Furthermore, mean particle diameter is a thing within the limits which are 0.03–0.3 micrometers, and since the pore of the particle aggregate formed on recorded media is easy to be formed effectively in the pore-radius field made into the purpose, such a particle has it. [preferably desirable]

[0109] (The pore physical properties and configuration of an anionic particle) An anionic particle which is used by this invention and which was described above has that desirable whose total pore volume the maximum pore radius of the particle by the nitrogen adsorption ****ing method is 2–12nm, and is 0.3 or more ml/g when making color material stick to the front face of the particle itself efficiently at the same time it forms efficiently the pore of the particle aggregate formed on recorded media again. The maximum pore radius of a particle is 3–10nm more preferably, and since the pore of the particle aggregate formed on recorded media is easy to be formed effectively in the pore-radius field made into the purpose, that whose total pore volume is 0.3 or more ml/g is desirable.

[0110] When the adsorption site of the color material on the front face of a particle exists enough that it is within the limits the BET specific surface area of whose is 70–300m²/g, the particle used by this invention becomes easy to leave color material near the front face of recorded media in the state of a single molecule more effectively, and contributes to color-enhancing improvement.

[0111] Moreover, the configuration of the particle used by this invention can make ion exchange water able to distribute a particle, can be dropped on a collodion membrane, can produce a test sample, and can observe and ask for it with a transmission electron microscope. In case a particle aggregate is made to form on recorded media in this invention, it is the point of making pore forming in an aggregate, and a non-globular form thing, such as the shape of the shape of a needle, a monotonous configuration or the shape of a rod which forms the aggregated particle connected with directivity with a spherical primary particle, or a necklace, can be suitably used for a particle. According to this invention persons' knowledge, since the dispersibility to water becomes [a needlelike twist / the orientation of a particle] random when the plate-like configuration is better and it forms a particle aggregate and pore volume becomes large, a particle is more desirable.

[0112] The content in the liquid constituent of an anionic particle which was described above is the range suitable when considering as the range of 0.1 – 40 mass % although what is necessary is just to determine the optimal range suitably attains the purpose of this invention according to the class of matter to be used, and the range of one to 30 mass %, and further 3 – 15 mass % is more preferably suitable for it. At such within the limits, it is not based on a medium kind, but the image of outstanding coloring can be obtained to stability, and it excels also especially in the preservation stability and regurgitation stability of a liquid constituent.

[0113] (Base) As stated previously, as for the anionic liquid constituent of this invention, it is desirable that pH is adjusted to 7-12 including a base. A base ionizes an anionic particle front face, and it plays the role of the viscosity control of the adsorption disposition top of the cationic compound in ink (cationic color material), or a liquid constituent while raising the distributed stability of the anionic particle in the inside of liquid by raising surface potential. When the base used suitable for this invention is combined with the anionic particle to be used, if physical properties, such as desired pH, F-potential, and particle dispersibility, are acquired, there is especially no limitation, and it can be used, choosing it to an inorganic compound, an organic compound, etc. which are listed below freely.

[0114] Specifically For example, a sodium hydroxide, a lithium hydroxide, a sodium carbonate, An ammonium carbonate, ammonia, sodium acetate, ammonium acetate, A morpholine, monoethanolamine, diethanolamine, triethanolamine, Ethyl monoethanolamine, n-butyl monoethanolamine, dimethylethanolamine, Alkanolamines, such as diethyl ethanolamine, ethyl diethanolamine, n-butyl diethanolamine, dinormal butyl ethanolamine, monoisopropanolamine, diisopropanolamine, and tri-isopropanolamine, can be used. Also in these, especially, since especially five or less base excels [dissociation constant / pkb / underwater / of a base / primary] in the distributed stability of an anionic particle, or adsorbent [of a cationic compound (cationic color material)], it is used suitably.

[0115] On mass criteria, it is the range of 150:1-8:1 more preferably, and A:B=200:1-5:1 and since it excels in the distributed stability of an anionic particle, and adsorbent [of the cationic compound on this front face of a particle], the mixed ratio of the anionic particle (A) in the inside of the liquid constituent of this invention and a base (B) is desirable.

[0116] (Other constituents) Next, the component of others which constitute an anionic liquid constituent is explained concretely. The anionic liquid constituent of this invention uses the above-mentioned anionic particle as an indispensable component. Although water is usually included as a solvent object, including a base which was preferably described above Furthermore, additives, such as the organic solvent mentioned by the term of the above-mentioned cationic liquid constituent and other additives, for example, a viscosity controlling agent, pH regulator, antiseptics, various surface active agents, an anti-oxidant, an evaporation accelerator, a water-soluble anionic compound, and binder resin, may be blended suitably. Moreover, as mentioned later, it is a desirable gestalt in the preservation stability of a liquid constituent and ink to add a photopolymerization initiator and a sensitizer in a liquid constituent at the same time it promotes hardening of a monomer efficiently.

[0117] (Surface tension of a liquid constituent) The anionic liquid constituent of this invention may be toned according to the color of recorded media, although it is more desirable to be colorlessness or that it is white. Furthermore, as suitable range of the various physical properties of the above liquid constituents, surface tension is more preferably made into 10 - 40 mN/m (dyn/cm) ten to 60 mN/m (dyn/cm), and viscosity is made into 1 - 30 mPa-s (cP).

[0118] (The manufacture approach of a liquid constituent) As the manufacture approach of the liquid constituent of this invention containing the aforementioned cationicity or an anionic particle, it can choose suitably from the approaches generally used for distribution, and can use. In order to make the mean particle diameter and particle size distribution of a particle in a liquid constituent into the above-mentioned range, using dispersers, such as a roll mill, a sand mill, a homogenizer, an ultrasonic homogenizer, and extra-high voltage emulsifiers (for example, trade name nano mizer etc.), the classification processing by distributed processing, centrifugal separation, ultrafiltration, etc. is used suitably, and, specifically, can arrange the diameter of a particulate material of the particle in a liquid constituent with these processing means.

[0119] Energy grant explains a polymerization and the polymerization nature component (monomer) which constructs a bridge as an indispensable component contained in <water-color-ink> ink.

[0120] (Polymerization nature component) - ink in this invention contains the solvent which dissolves the polymerization nature component (monomer) and this monomer which are converted into the cross linked polymer by grant of energy other than the color material mentioned later as an indispensable component. The purpose using this monomer sticks the

coloring section with recorded media, is enclosing color material by the crosslinked polymer formed of the energy grant to a monomer with the particle, and is to raise the scratch-proof nature and weatherability of the coloring section while making the coloring section form on the scarce recorded media of absorbency, such as a plastics metallurgy group, at stability as the term of a mechanism described. In addition, in this invention, a monomer may call it hardening a polymerization and to construct a bridge and to convert into the cross linked polymer by energy grant.

[0121] As a monomer hardened by grant of the energy used for the liquid constituent of this invention, the acrylic (meta) monomers of radical polymerization nature and the epoxy monomers which suit a cationic polymerization system can use it suitably. As acrylic (meta) monomers of radical polymerization nature, the following monomer is mentioned, for example.

[0122] Specifically (1) N and N-dimethylaminoethyl methacrylate $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (2) N, N-dimethylamino ethyl acrylate $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (3) 2 N, N-dimethylaminopropyl methacrylate $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (4) N, NN[- dimethylaminopropylacrylate $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2\text{CH}_2\text{CH}_2$] $(\text{CH}_3)_2$ (5) 2 N, N-dimethylamino acrylamide $\text{CH}_2=\text{CH}-\text{CON}(\text{CH}_3)_2$ (6) 2 N, and N-dimethylamino meta-acrylamide $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CON}(\text{CH}_3)_2$ (7) N, N-dimethylaminoethyl acrylamide $\text{CH}_2=\text{CH}-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2$ (8) N, N-dimethylaminoethyl meta-N[acrylamide $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONHC}_2\text{H}_4$] $(\text{CH}_3)_2$ (9) 2 N, N-dimethylaminopropyl acrylamide $\text{CH}_2=\text{CH}-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2$ (10) N, N-dimethylaminopropyl methacrylamide $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2$, these monomers formed into 4 class Color-material dyeing property, It excels in the film strength and is especially desirable.

[0123] Moreover, the well-known ultraviolet curing mold monomers and the oligomer of the acrylic ester (meta) of polyhydric alcohol, the acrylic ester (meta) of the glycidyl ether of polyhydric alcohol, the acrylic ester (meta) of a polyethylene glycol, the acrylic ester (meta) of the ethylene oxide addition product of polyhydric alcohol, and a polybasic acid anhydride and hydroxyl-group content (meta) acrylic ester, such as a reactant, are used. The high matter of the compatibility in the inside of a liquid constituent out of these monomers or a hydrophilic property is chosen, and it is used. As epoxy monomers which suit a cationic polymerization system, the glycidyl ether of polyhydric alcohol, glycidyl ester, aliphatic series annular epoxide, etc. are used, for example.

[0124] In this invention, when a pigment is used especially for ink as a color material and ultraviolet rays are used as hardening energy, the cure rate of a monomer tends to become slow. Therefore, as a polymerization system of a (ultraviolet-rays UV) polymerization monomer, the monomer of a high Brit polymerization system is desirable, and, subsequently to order, it is desirable to select the monomer of a cationic polymerization system and a free radical polymerization system.

[0125] The content of the monomer contained in the liquid constituent in this invention usually has the desirable range of 1 - 50 mass %. The hardenability of under 1 mass % is inadequate, and since the viscosity of a constituent will rise and dischargeability will worsen if weatherability, solvent resistance, scratch-proof nature, and adhesion will become low and 50 mass % is exceeded, a generation polymer is not desirable. It is three to 40 mass % preferably, and is choosing a monomer in this range, and in this range, there is an advantage that the liquid constituent which is compatible in hardenability and dischargeability is obtained, and it is five to 30 mass % still more preferably, and since dischargeability is also satisfactory, it has [hardenability is enough, and] the advantage to which the selectivity of a monomer spreads.

[0126] (A photopolymerization initiator and sensitizer) When using ultraviolet-rays energy for hardening of the monomer in ink in this invention, it is desirable to use a photopolymerization initiator. As a photopolymerization initiator, a carbonyl compound, an azo compound, organic peroxide, etc. are mentioned, for example. as a usage — a photopolymerization initiator — one kind — or even if it uses two or more kinds, it does not matter even if it uses a photopolymerization initiator and a sensitizer together. It is not restricted especially that what is necessary is just to select suitably about selection of the main photopolymerization initiators and sensitizers, combination, and a compounding ratio with the ultraviolet-rays polymerization nature monomer and the equipment used to be used.

[0127] As main photopolymerization initiators, for example, acetophenone, 2, and 2-diethoxy acetophenone, p-dimethylamino acetophenone, p-dimethylamino propiophenone, A benzophenone, 2-chlorobenzophenone, p, and p'-dichloro benzophenone, A p and p'-bis-diethylamino benzophenone, a Michler's ketone, benzyl (diphenyl diketone), A benzoin, benzoin methyl ether, benzoin ethyl ether, Benzoin iso-propyl ether, the benzoin-n-propyl ether, Benzoin isobutyl ether, benzoin-n-butyl ether, Benzyl dimethyl ketal, tetramethylthiuram monosulfide, Thioxanthone, 2-chloro thioxanthone, 2-methylthioxanthone, Azobisisobutyronitril, benzoin peroxide, G tert-butyl peroxide, 1-hydroxy cyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenyl-1-ON, 1-(4-isopropyl phenyl)-2-hydroxy-isobutane-1-ON, a methyl benzoyl FO mate, etc. are mentioned. The amount of these photopolymerization initiators used is usually 0.1 to 10 mass % to the total amount of an ultraviolet-rays hardenability monomer.

[0128] Moreover, in a cationic polymerization mold, photoinitiators, such as aromatic series diazonium salt, an aromatic series halo NIUMU salt, aromatic series sulfonium salt, and a metallocene compound, are used. Triphenylsulfonium hexafluoro phosphate, diphenyliodonium hexafluoroantimonate, etc. are mentioned as the example. Moreover, in the case of a cationic polymerization mold, in order to make hardening still more perfect, it is the range of 80-170 degrees C, and it is desirable to heat in 100-150 degrees C desirably especially. Although heating time changes with conditions, it is usually for 5 - 30 minutes.

[0129] The amine which contains 1. amine system: fatty amine and an aromatic series radical as a sensitizer, for example, A piperidine, 2. urea: allyl compound system, o-tolyl thiourea, 3. sulfur compound : Sodium diethyl dithiophosphate, A fusibility salt [of an aromatic series sulfinic acid], 4. nitril system compound: N, and N-Jl permutation-p-amino benzonitrile, 5. — phosphorus-compounds: — tri-n-butyl phosphine and NETORIUMU diethyl JICHIOHOSU feed — 6. — nitride: — a Michler's ketone and N-NITORISO hydroxylamine derivative — An oxazolidine compound, tetrahydro - 1, 3-oxazine compound, Formaldehyde or an acetaldehyde, the condensate of diamine, 7. chlorine compound: A carbon tetrachloride, hexachloroethane, the macromolecule-ized amine of the resultant of 8. epoxy resin and an amine, a triethanolamine thoria chestnut rate, etc. are mentioned.

[0130] Although the above-mentioned photopolymerization initiator and a sensitizer can be included in both a liquid constituent, or both [either or], since the preservation stability of a liquid constituent becomes still higher by making it contain in an ink side and making it dissociate with a monomer especially, they are desirable. When using an electron ray as hardening energy, especially the above-mentioned photopolymerization initiator or the above-mentioned sensitizer are not needed. Moreover, there is also no exposure inhibition by the pigment, and since [with few temperature rises] a cure rate is also quick, as the hardening approach of the monomer of this invention, it is effective.

[0131] [Anionic ink], next the water anionic ink which constitutes the ink set of this invention combining the cationic liquid constituent explained by the above are explained. Combination with at least one sort of anionic ink in which an ink set here contains the liquid constituent and anionic matter (anionic color material) of this invention is said. Moreover, the combination of at least one kind of ink except the liquid constituent of this invention is called an ink subset from this ink set.

[0132] When using a pigment as a color material, using the water soluble dye which contains an anionic radical as a color material, as for the anionic ink used by this invention, it is desirable to use the thing (for this to also be called anionic color material by this invention) which made the anionic compound use together. Water, a water-soluble organic solvent and other components, for example, a viscosity controlling agent, pH regulator, antiseptics, a surfactant, an antioxidant, etc. are further contained and constituted by the above anionic ink used by this invention at this if needed. Hereafter, each constituent of these ink is explained.

[0133] (Water soluble dye) As water soluble dye which has the anionic radical used by this invention, especially if it is the water-soluble acid dye indicated by the Color Index (it may abbreviate to C.I. below by Color Index:), direct dye, and reactive dye, it will not be limited, for example. Moreover, what does not have a publication in a Color Index will not be limited especially if it has an anionic radical, for example, a sulfone radical, a carboxyl group, etc. A thing

with the pH dependency of solubility is also contained in water soluble dye here.

[0134] (Pigment) You may be ink which uses a pigment and an anionic compound and contains water, a water-soluble organic solvent and other components, for example, a viscosity controlling agent, pH regulator, antiseptics, a surfactant, an antioxidant, etc. as another gestalt of water anionic ink instead of the water soluble dye which has the above anionic radicals if needed. Here, an anionic compound may be the dispersant of a pigment, and when the dispersant of a pigment is not anionic, what added the anionic compound different from a dispersant may be used. Of course, even when a dispersant is an anionic compound, what added the anionic compound of further others may be used.

[0135] Although there is especially no limitation in the pigment which can be used by this invention, the pigment explained below can use it suitably, for example. First, as carbon black used for black pigment ink, it is carbon black manufactured with the furnace method or the channel process, and that in which 40-150ml / 100g, and volatile matter have 0.5 to 10 mass %, and a pH value has [a specific surface area according / primary particle size / to 15 - 40mmum and a BET adsorption method / 50-300m²/g and DBP oil absorption] 2-9 is desirable.

[0136] As such a thing, they are No.2300, No.900, MCF88, No.40, No.52, MA7 and MA8, and No.2200B (above), for example. Mitsubishi Chemical make : RAVEN 1255(made in Colombia):REGAL 400R, REGAL 660R, MOGUL L (above) Cabot make: Color Black FW1, Color Black FW18, Color Black S 170, Color Black S 150, Printex 35, Printex U (above) Commercial items, such as the Degussa make, can be used. Moreover, a prototype could newly because of this invention be built.

[0137] As a pigment used for yellow ink, it is C.I.Pigment Yellow, for example. 1, C.I.Pigment Yellow 2, C.I.Pigment Yellow 3, C.I.Pigment Yellow 13, C.I.Pigment Yellow 16, and C.I.Pigment Yellow 83 grade are mentioned.

[0138] As a pigment used as Magenta ink, C.I.Pigment Red 5, C.I.Pigment Red 7, C.I.Pigment Red 12, and C.I.Pigment Red 48(calcium) C.I.Pigment Red 48 (Mn) and C.I.Pigment Red 57(calcium) C.I.Pigment Red112 and C.I.Pigment Red 122 grade are mentioned, for example.

[0139] As a pigment used as cyanogen ink, it is C.I.Pigment Blue, for example. 1, C.I.Pigment Blue 2, C.I.Pigment Blue 3, C.I.Pigment Blue 15:3, C.I.Pigment Blue 16, C.I.Pigment Blue 22, C.I.Vat Blue 4, and C.I.Vat Blue 6 grade are mentioned. moreover, the above — what was newly manufactured also about the color material of which color for this invention is usable.

[0140] (Pigment agent) Anythings are usable if it is water soluble resin which has the function to make water or an aquosity medium distribute a pigment to stability, by existence of an anionic radical as a dispersant of the pigment which can be used for the ink used by this invention. Especially, the thing of the range of 1,000-30,000 has desirable weight average molecular weight. Furthermore, the range of weight average molecular weight is 3,000-15,000 preferably. The salt of the block copolymer which specifically consists of two or more monomers chosen from a hydrophobic monomer or an acrylic acid, an acrylic-acid derivative, a maleic acid, a maleic-acid derivative, an itaconic acid, an itaconic-acid derivative, a fumaric acid, and fumaric-acid derivatives, such as fatty alcohol ester of styrene, styrene derivative, vinyl naphthalene, vinyl naphthalene derivative, alpha, and beta-ethylene nature unsaturated carboxylic acid, a graft copolymer, random copolymers, or these (**) polymers etc. is mentioned. These resin is resin of an alkali meltable mold meltable in the water solution in which the base was dissolved.

[0141] Furthermore, the homopolymers which consist of a hydrophilic monomer, or those salts are sufficient. Moreover, it is also possible to also use water soluble resin, such as polyvinyl alcohol, a carboxymethyl cellulose, and a naphthalene sulfonic-acid formaldehyde condensate. However, the direction at the time of using the resin of an alkali meltable mold is possible for hypoviscosity-izing of dispersion liquid, and there is an advantage that distribution is also easy. As for said water soluble resin, it is desirable to be used in the range of 0.1 - 5 mass % to the ink whole quantity.

[0142] In the pigment and water soluble resin like ****, in a water-soluble medium, it distributes or dissolves and the pigment ink which can be used by this invention is constituted. In the pigment ink which can be used for this invention, it is the mixed solvent of water and a water-soluble organic solvent as a suitable aquosity medium, and it is desirable to use not the common

water that contains various ion as water but ion exchange water (deionized water).

[0143] When a dispersant is not an anionic macromolecule, it is desirable to add an anionic compound further in the ink containing the pigment mentioned above. The anionic surfactant of low molecular weight which is listed to the following besides high polymers, such as alkali fusibility resin explained by the term of a pigment agent, as an anionic compound suitably used by this invention can be mentioned.

[0144] As the anionic surfactant of low molecular weight being concrete For example, sulfo succinic-acid lauryl disodium, sulfo succinic-acid polyoxyethylene lauroyl ethanol AMIDOESUTERU disodium, Polyoxyethylene alkyl sulfo succinic-acid disodium, carboxylation polyoxyethylene lauryl ether sodium salt, Carboxylation polyoxyethylene tridecyl ether sodium salt, Although polyoxyethylene lauryl ethereal sulfate sodium, polyoxyethylene lauryl ethereal sulfate triethanolamine, a polyoxyethylene-alkyl-ether sodium sulfate, sodium alkylsulfate, alkyl-sulfuric-acid triethanolamine, etc. are mentioned It is not limited to these. The suitable amount of the above anionic matter used is the range of 0.05 - 10 mass % to the ink whole quantity, and is 0.05 to 5 mass % still more suitably.

[0145] (Self-distributed pigment) As a pigment which can be used for anionic ink, the pigment of self-distributed process input output equipment which water or an aquosity medium can be made to distribute can also be used again, without using a dispersant. As for the pigment of self-distributed process input output equipment, at least one sort of anionic hydrophilic radicals are combined with the pigment front face through direct or other atomic groups. The naphthylene radical on which at least one sort chosen from the next hydrophilic radicals as an anionic hydrophilic radical, for example and the atomic group of further others may have the phenylene group which may have the alkylene group of the carbon atomic numbers 1-12 and a substituent, or a substituent is mentioned.

- COOM, -SO₃M, -SO₂NH₂, -PO₃HM, -PO₃M₂ (M in the above-mentioned formula expresses a hydrogen atom, alkali metal, ammonium, or organic ammonium.)

[0146] Thus, since the pigment which electrified anionic by installation of the hydrophilic radical on the front face of a pigment has water-dispersion [which was excellent with repulsion of ion], it maintains the distributed condition stabilized even if it did not add a dispersant etc., also when it was made to contain in water color ink. It is desirable when especially a pigment is carbon black.

[0147] (Addition component in ink) In order to consider as the ink which has a desired physical-properties value other than the above-mentioned component if needed again, a surfactant, a defoaming agent, or antiseptics can be added in ink, and commercial water soluble dye etc. can also be added further.

[0148] As a surfactant, nonionic surfactants, such as anionic surfactants, such as fatty-acid salts, higher-alcohol sulfate salts, liquid fatty-oil sulfate salts, and alkyl allyl compound sulfonates, polyoxyethylene alkyl ether, polyoxyethylene alkyl ester, polyoxyethylene sorbitan alkyl ester, acetylene alcohol, and an acetylene glycol, are mentioned, and these one sort or two sorts or more can be used, for example, choosing them suitably. Although the amount used changes with additions of a dispersant, its 0.01 - 5 mass % is desirable to the ink whole quantity. Under the present circumstances, it is desirable to determine the addition of a surfactant that the surface tension of ink will become more than 30 mN/m (dyn/cm). In the ink jet recording method used by this invention, it is because generating of the printing kink (gap of the impact area of an ink droplet) at the tip of a nozzle depended for getting wet can be suppressed effectively.

[0149] After adding and stirring a pigment first as the production approach of pigment ink which was explained above in the water solution which contains the resin for pigment-content powder, and water at least, for example, distributed processing is performed using the below-mentioned distributed means, centrifugal separation processing is performed if needed, and desired dispersion liquid are obtained. Next, what is necessary is to add further a component which was hung up over these dispersion liquid above, to stir it, and just to consider as ink.

[0150] Moreover, in using the resin of an alkali meltable mold, in order to dissolve resin, it requires adding a base. Under the present circumstances, the amine for dissolving resin or the

amount of a base needs to add 1 or more times of the amine called for by count from the acid number of resin, or the amount of bases. The amount of an amine or a base is calculated by count by the following formulas.

アミン或いは塩基の量 (g)

$$= \frac{(\text{樹脂の酸価} \times \text{アミン或いは塩基の分子量} \times \text{樹脂量 (g)})}{5600}$$

5600

[0151] Furthermore, if pre mixing is performed more than for 30 minutes before carrying out distributed processing of the water solution containing a pigment, the distributed effectiveness of a pigment will become good. This pre mixing actuation improves the wettability on the front face of a pigment, and promotes adsorption of the dispersant on the front face of a pigment.

[0152] As bases added by the dispersion liquid at the time of using alkali meltable mold resin, it is desirable to, use inorganic bases, such as organic amines, such as monoethanolamine, diethanolamine, triethanolamine, amine methyl propanol, and ammonia, or a potassium hydroxide, and a sodium hydroxide, for example.

[0153] On the other hand, although what kind of thing may be used if the disperser used for preparation of pigment ink is a disperser generally used, a ball mill, a sand mill, etc. are mentioned, for example. Also in it, the sand mill of a high-speed mold is desirable, for example, a super mill, a Sand grinder, a bead mill, an agitator mill, a grain mill, a die Norian mill, a pearl mill, the COBOL mill (all are trade names), etc. are mentioned.

[0154] [Cationic ink], next the water cationic ink which constitutes the ink set of this invention combining the anionic liquid constituent explained previously are explained. Combination with at least one sort of ink in which an ink set here contains the liquid constituent and cationic matter (cationic color material) of this invention is said. Moreover, the combination of at least one sort of ink except the liquid constituent of this invention is called an ink subset from this ink set.

When using a pigment as a color material as a color material, using the water soluble dye containing a cationic radical, as for the cationic ink used by this invention, it is desirable to make a cationic compound use together (for this concomitant use to also be called cationic color material in this invention). Water, a water-soluble organic solvent and other components, for example, a viscosity controlling agent, pH regulator, antiseptics, a surfactant, an antioxidant, etc. are further contained and constituted by the above ink used by this invention at this if needed. Hereafter, each constituent of these ink is explained.

[0155] (Water soluble dye) As water soluble dye which has the cationic radical used by this invention, especially if it is the water-soluble color indicated by the Color Index, it will not be limited, for example. Moreover, if what does not have a publication in a Color Index has a cationic radical, there will be especially no limitation. In addition, a thing with the pH dependency of solubility is also contained in water soluble dye here.

[0156] (Pigment) You may be ink which uses a pigment and a cationic compound and contains water, a water-soluble organic solvent and other components, for example, a viscosity controlling agent, pH regulator, antiseptics, a surfactant, or an antioxidant if needed instead of the water soluble dye which has the above-mentioned cationic radical as another gestalt of the ink used by this invention. Here, a cationic compound may be the dispersant of a pigment, and when the dispersant of a pigment is not cationicity, what added the cationic compound different from a dispersant may be used. Of course, even when a dispersant is a cationic compound, the cationic compound of further others may be added. As a pigment which can be used by this invention, there is especially no limitation and it can use suitably the pigment stated by the term of anionic ink.

[0157] (Pigment agent) Anythings [its] are usable if the dispersant of the pigment in the ink used by this invention is water soluble resin which has the function to make water or an aqueous medium distribute a pigment to stability by existence of a cationic radical. Some polymers [at least] which are obtained by the polymerization of a vinyl monomer and are obtained as an example should just have cationicity. As a cationic monomer for constituting a cationic part, the salts and these compounds formed into 4 class of the tertiary amine monomer like the following are mentioned.

[0158] Specifically N and N-dimethylaminoethyl methacrylate $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]$, N and N-dimethylamino ethyl acrylate $[\text{CH}_2=\text{CH}-\text{COO}-\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]$, N and N-dimethylaminopropyl methacrylate $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$, N and N-dimethylaminopropylacrylate $[\text{CH}_2=\text{CH}-\text{COO}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$, N,N-dimethylacrylamide $[\text{CH}_2=\text{CH}-\text{CON}(\text{CH}_3)_2]$, N and N-dimethyl methacrylamide $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{CON}(\text{CH}_3)_2]$, N and N-dimethylaminoethyl acrylamide $[\text{CH}_2=\text{CH}-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2]$, N and N-dimethylaminoethyl methacrylamide $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2]$, N,N-dimethylaminopropyl acrylamide $[\text{CH}_2=\text{CH}-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$, N, and N-dimethylaminopropyl methacrylamide $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$

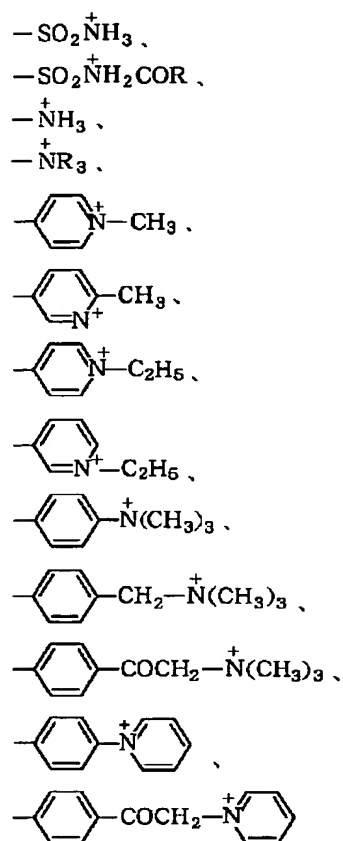
** is mentioned.

[0159] As a compound for forming a salt in the case of a tertiary amine monomer, a hydrochloric acid, a sulfuric acid, an acetic acid, etc. are mentioned, and a methyl chloride, a dimethyl sulfate, benzyl chloride, epichlorohydrin, etc. are mentioned as a compound used for the 4th class-ization, for example. Also in these, when a methyl chloride, a dimethyl sulfate, etc. prepare the dispersant used by this invention, it is desirable. Underwater, the salt or the 4th class ammonium compound of the above tertiary amine monomers is served as a cation, and acidity is a stable dissolution field on the neutralized conditions. The content in the inside of the copolymer of these monomers has the desirable range of 20 - 60 mass %.

[0160] In addition to this as a monomer, acrylamides, vinyl ether, vinyl pyrrolidone, vinylpyridines, and vinyl oxazoline are mentioned as a water-soluble monomer which can be dissolved in hydrophobic monomers, such as acrylic ester which has hydroxy groups, such as acrylic ester which is used for the configuration of the above-mentioned giant-molecule dispersant, and which has 2-hydroxyethyl methacrylate and a long-chain ethylene oxide chain in a side chain, for example, and a styrene system monomer, and with a pH of about seven water. As a hydrophobic monomer, hydrophobic monomers, such as styrene, a styrene derivative, vinyl naphthalene, a vinyl naphthalene derivative, alkyl ester of an acrylic acid (meta), and acrylonitrile, are used. In order that a water-soluble monomer may make a copolymer exist in stability in a water solution in the macromolecule dispersant obtained by copolymerization, it uses in the range of 15 - 35 mass %, and in order to heighten the dispersion effect over the pigment of a copolymer, as for a hydrophobic monomer, it is desirable to use in the range of 20 - 40 mass %.

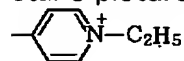
[0161] (Self-distributed pigment) In the case of the pigment charged in cationicity, that with which the hydrophilic radical combined through direct or other atomic groups combined at least one chosen from the next 4th class ammonium is mentioned. However, this invention is not limited to these.

[0162]



[0163] R expresses the naphthyl group which is not permuted [the phenyl group which is not permuted / the shape of a straight chain of the carbon atomic numbers 1-12, a branched-chain alkyl group, a permutation, or /, a permutation, or] among the above-mentioned formula. In addition, for example, NO_3^- and CH_3COO^- exist in the above-mentioned cationic radical as counter ion.

[0164] If it explains taking the case of the approach of combining N-ethyl pyridyl radical of the structure shown below, for example as an approach of manufacturing the self-distributed pigment which a hydrophilic radical which was described above was combined and has been charged in cationicity, the method of processing a pigment with a 3-amino-N-ethyl pyridinium star's picture will be mentioned.



[0165] Thus, since the pigment which electrified cationicity by installation of the hydrophilic radical on the front face of a pigment has water-dispersion [which was excellent with repulsion of ion], it maintains the distributed condition stabilized even if it did not add a dispersant etc., also when it was made to contain in water color ink. The case where especially the above-mentioned pigment is carbon black is desirable.

[0166] The cationic ink further used by this invention is adding said surfactant from the field which makes good the permeability of the ink to recorded media, and matching of as opposed to [get wet, simultaneously] the head for ink jets. (Surface tension of ink) It is desirable to adjust the surface tension in 25 degrees C to 30 - 68 mN/m (dyn/cm) as physical properties of ink itself, and to adjust viscosity to below 5 mPa-s (cP) more preferably below 10 mPa-s (cP) below 15 mPa-s (cP).

[0167] (Other components contained in ink) In addition, the ink used by this invention may add additives other than the above-mentioned component, such as a water-soluble organic solvent, a surface active agent, pH modifier, a rust-proofer, an antifungal agent, an antioxidant, an evaporation accelerator, a chelating agent, and a water-soluble polymer, if needed.

[0168] As for the solvent object which dissolves or distributes the above-mentioned monomer which can be used by this invention, it is desirable that it is the mixture of water and a water-soluble organic solvent. As a water-soluble concrete organic solvent, for example Methyl alcohol, ethyl alcohol, N-propyl alcohol, isopropyl alcohol, n-butyl alcohol, Alkyl alcohols of the carbon numbers 1-4, such as sec-butyl alcohol and tert-butyl alcohol : Dimethylformamide, amides [, such as dimethylacetamide,] : — ketones [, such as an acetone,] : — a tetrahydrofuran — Ether, such as dioxane : Polyalkylene glycols:ethylene glycol, such as a polyethylene glycol and a polypropylene GUKORI call, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, and 6-KISAN triol and thiodiglycol — passing — a xylene glycol — The alkylene glycol in which alkylene groups, such as a diethylene glycol, contain 2-6 carbon atoms : A glycerol, The low-grade alkyl ether of polyhydric alcohol, such as the ethylene glycol monomethyl (or ethyl) ether and the diethylene-glycol monomethyl (or ethyl) ether : A N-methyl-2-pyrrolidone, Imide compounds, such as cyclic amide compounds, such as 1,3-dimethyl-2-imidazolidinone, a sulfolane, dimethyl sulfoxide, 2-pyrrolidone, and epsilon caprolactam, and a succinimide, etc. are mentioned.

[0169] Generally, 1 - 40% of the content of the water-soluble above-mentioned organic solvent is desirable to the total mass of ink, and is 3 - 30% of range more preferably. Moreover, when it is made into the range of 30 - 95 mass %, the content of the water in ink is good, and since it can suppress that the viscosity of ink becomes high and can fully satisfy a fixing property, it is desirable. [of the solubility of color material]

[0170] Although the ink used by this invention can be used also as ink of common aquosity writing materials, especially when applying to the ink jet record approach of a type of making ink breathing out according to the foaming phenomenon of the ink by heat energy, it is suitable, and it becomes very stable [the regurgitation], and there is the description that generating of a satellite dot etc. does not arise. However, a thermal physical-properties value (for example, the specific heat, a coefficient of thermal expansion, thermal conductivity) may be adjusted in this case.

[0171] Although the concentration of the color-material component contained in the anionic and cationic ink of which the <concentration of water color ink> above was done is suitably chosen according to the class of color material, such as an aquosity color, a pigment, and a self-distributed pigment, 0.1 - 12% of its range is especially desirable 0.1 to 20% to the total mass of ink. Moreover, especially the color enhancement of the image with which the concentration of a color-material component is formed under the record conditions of the usual 2 liquid system when color material takes especially or less for 1.0 1.2 or less to this particle 1 on mass criteria, concerning the relation between the concentration of the particle in a liquid constituent and the concentration of the color material in ink in the range of 0.3 - 7 mass % becomes the outstanding thing.

[0172] The <approach of forming the coloring section in recorded media>, next the approach of forming the coloring section in the recorded media of this invention are explained. The approach of forming the coloring section in the recorded media of this invention (i) The solvent which dissolves the monomer and this monomer which carry out a polymerization by grant of color material and energy is included. It has the process which gives the liquid constituent which contains the particle to which the front face is charged in a polarity contrary to the process and (ii) this ink which give anionic or cationic ink to recorded media in the state of distribution to recorded media. It is characterized by giving ink and a liquid constituent to the front face of the above-mentioned recorded media so that it may touch in the state of a liquid mutually. How to give the liquid constituent and ink which are hereafter constituted as mentioned above on recorded media is explained.

[0173] The approach of forming the coloring section in the recorded media of this invention includes the process (i) containing the process (ii) which gives a liquid constituent which was explained above on recorded media, and the solvent which dissolves the monomer and this monomer which carry out a polymerization by grant of color material and energy which gives anionic or cationic ink to recorded media. Although a liquid constituent is given to the coloring section formation field of the recorded media formed in the ink which contains color material in

that case or a coloring section formation field, and its near, ink and a liquid constituent are given so that they may touch in the state of a liquid mutually. A coloring section formation field here is a field where the dot of ink adheres, and the thing of the field which about 1-5 dots of outsides of the field where the dot of ink adheres left is pointed out near the coloring section formation field.

[0174] As long as it is the approach the above mentioned liquid constituent and the ink of this invention come to touch the recorded media of this invention in the state of a liquid mutually on recorded media by the approach of forming the coloring section, these may be made to give by which approach. Therefore, it is not a problem any shall be previously given on recorded media between a liquid constituent and ink. For example, after performing a process (i) after performing a process (ii), and performing a process (i), ***** is also good in a process (ii). Moreover, after performing a process (i), it is also desirable to perform a process (ii) and to perform a process (i) again after that. Moreover, when a liquid constituent is made to give previously recorded media, it is not restricted especially about time amount after giving a liquid constituent to recorded media until it makes ink give on recorded media, but in order to make it touch in the state of a liquid mutually, it is desirable to make ink give within coincidence or several seconds on recorded media mostly.

[0175] Next, also about the timing which gives the energy which stiffens the monomer in ink, if it is after giving the both sides of ink and a liquid constituent, it can choose freely [always]. However, after forming the pixel of the last liquid constituent, it is necessary to surely give energy and to harden a monomer. Moreover, when giving energy about removal of the solvent in a liquid constituent and ink, i.e., desiccation, it is desirable that almost all solvents are removed. As a desiccation means, it is desirable to put a base material (recorded media) into an air-heating furnace with a temperature of about 50-200 degrees C. However, the polymerization of a monomer etc. may be performed in the condition of not removing a solvent from the purpose of compaction of the processing time completely, and you may dry later. Anyway, since the good thing of image physical properties is not obtained, it is not desirable that the solvent remains in the last image formation object. Moreover, as for the energy grant as a means to harden a monomer, UV irradiation, electron beam irradiation, heat radiation, etc. are mentioned as mentioned above. For example, it is desirable to irradiate about two 200 - 1000 mJ/cm ultraviolet rays in addition, using a high pressure mercury vapor lamp as a UV irradiation means. The range of the emission spectrum of the ultraviolet-rays field of the mercury lamp of the above-mentioned high pressure mercury vapor lamp is 184nm - 450nm, and it is suitable for stiffening an ultraviolet-rays hardenability monomer efficiently. Moreover, when using electron-beam-irradiation equipment, it is desirable to irradiate in the range of 1 - 50Mrad.

[0176] (Recorded media) Especially the recorded media used for the approach of forming the coloring section in the recorded media of above-mentioned this invention are not limited, and various objects, such as the so-called regular papers, such as a copy paper currently used from the thing of the absorbency scarce quality of the materials, such as art paper for printing, plastics, a metal, and a tile, and the former and bond paper, are used suitably. Of course, the coat paper and the bright film for OHP which were specially produced to ink jet record are also used suitably. Furthermore, common paper of fine quality and glossy paper can also be used suitably.

[0177] (The grant approach of a liquid constituent) Although how to make it give all over recorded media with a spray, a roller, etc. is also considered, for example as an approach of making the liquid constituent of this invention give on recorded media Furthermore, it is desirable alternative only near the coloring section formation field which gives ink preferably or a coloring section formation field, and its coloring section formation field, and that the ink jet method which can make a liquid constituent give homogeneity performs. Moreover, although various ink jet recording methods can be used in this case, especially a desirable thing is a method which carries out the regurgitation of the drop using the air bubbles generated with heat energy.

[0178] A <ink jet recording apparatus>, next the ink jet recording apparatus of this invention are explained. The ink hold section in which the ink jet recording device of this invention contains the solvent which dissolves the monomer and this monomer which carry out a polymerization by

grant of color material and energy and which held anionic or cationic water color ink, It is characterized by having the 1st record unit equipped with the ink jet head which makes this ink breathe out, the liquid constituent hold section which held the liquid constituent of said this invention, and the 2nd record unit equipped with the ink jet head which makes this liquid constituent breathe out.

[0179] Especially the ink jet recording device that can be used for the ink jet record approach of this invention It is the ink jet recording device which gives a liquid constituent and the ink of at least one or more colors from the recording head equipped with two or more ink deliveries also to recorded media without ink absorptivity, and forms a record image. a) The means which carries out defecation processing of said recorded-media front face, the recording head equipped with two or more ink deliveries which an ink droplet is made to fly according to b image recording signal, and give an ink droplet to the predetermined location on said front face of recorded media, and a means to stiffen the ink droplet of the c aforementioned image formation are provided.

[0180] In the ink jet recording device concerning this invention, the means of a may be omitted depending on recorded media. Moreover, as technique, UV/O₃ washing is mentioned, for example. As a hardening means of the ink droplet of c), a UV irradiation lamp, EB (electron ray) exposure, heat, etc. are mentioned. In a UV irradiation lamp, since heat may occur and recorded media may deform, it is desirable that a cooler style, for example, a cold mirror, a cold filter, work-piece cooling, etc. possess.

[0181] Drawing 1 is the typical schematic diagram showing the whole ink jet recording device. 110 in drawing 1 is a recording head, and is the ink jet recording head by which 300 nozzle x5 train of 600dpi was arranged together with one. As a liquid constituent and ink, five heads for four classification by color of Y (yellow), M (Magenta), C (cyanogen), and Bk (black) are prepared, and the above-mentioned recording head is set so that a full color image can be recorded by one scan. 101 is recorded media. The recorded media 101 of two or more sheets are set to the stocker 111, and it is sent to a band conveyor 113 by the conveyance machine 112, and is sent out to the tray 115 for printing. 114 is an auxiliary roller for sending recorded media.

[0182] Adsorption immobilization of the recorded media 101 sent to the tray 115 for printing is firmly carried out by suction with a pump 116 on a tray. The recorded media 101 on the tray 115 for printing are sent into the field to which the 1st processing process is performed. 104 is UV/O₃ lamp. With recorded media, when surface wettability is low, surface treatment of recorded media is performed and the wettability of ink and adhesion are raised. This processing process may be passed (abbreviation).

[0183] Shortly after recorded media are taken out from the field of the 1st process by the delivery motor of 111, ink jet record by the recording head 110 is performed. Although various ink jet recording methods, such as a piezo method and an electrostatic method, can be used for ink jet record which is this 2nd process, the bubble jet (trademark) method which is stabilized and can perform high-speed record is suitable.

[0184] Moreover, if it seems that problems, such as a blot, occur in one-pass printing also as the record approach, a two pass and 4 pass printing will be adopted. The recorded media with which the image was recorded are immediately conveyed to the field to which solidification of the 3rd process is performed. Here, 105 is a UV irradiation lamp.

[0185] Since heat occurs and deformation of recorded media may be caused by the exposure of UV lamp, heating prevention devices, such as a cold mirror, a cold filter, and work-piece air cooling (un-[in a Fig.] illustrating above), are required.

[0186] The recorded media (it has a record image) which passed through the above three processing processes are conveyed by the stocker 119 through a band conveyor 120 and the delivery roller 121, and are contained by the predetermined location with a handler 118.

[0187] In the illustrated example, although recorded media 101 are the thing of a tabular configuration, the tray which conveys this is suitably adjusted so that it can respond to the configuration of recorded media. For example, correspondence also in record to the disc-like recorded media 101 is attained by using spacer 211 grade as shown in drawing 3. Moreover, as for this equipment, it is desirable to have a means to adjust the distance of a recording head and

the image formation side of recorded media according to the thickness of recorded media.

[0188] Moreover, in order to promote the heat hardening (bridge formation of a polymer) in the 1st process and 3rd process, by forming heating means, such as a heater, in a tray auxiliary, for example, heating recorded media before each processing, heating effectiveness is raised even to processing of comparatively large-sized recorded media with big heat capacity, and effective processing is attained.

[0189] In addition, when it heat-treats to recorded media, and deviation arises in a dimension, a gap of the cross direction of record and a feed direction arises and problems, such as generating of the white stripe in a record image and gap of printing size, arise by thermal expansion, as shown in drawing 4 It compares with the value beforehand set up with the comparator after detecting the skin temperature of the image formation side of recorded media 401 with the thermo sensor 402, amplifying with the amplifier (Amp) and digitizing this with an A/D converter (A/D). It is desirable to use the system adjusted so that recorded media can be set to a recording head 410 and a motor 403 by the optimal delay signal over the signal of a clock to a signal at delivery and a right location.

[0190] Moreover, in order to make recorded media convey with a sufficient precision, marking of the mark can be carried out to the non-printing area of recorded media with etching or a press, the location can be read with a suitable read means, the location of recorded media can always be checked, a conveyance means can be controlled by the location, and more accurate conveyance can also be performed. Moreover, when curvature etc. is in recorded media, it is also effective in a roller etc. to add the function which corrects curvature because of [, such as curvature,] amendment. Moreover, what is necessary is just to remove this with the means of a shirring press etc. after printing, if the aforementioned mark spoils product value.

[0191] Drawing 2 is the typical schematic diagram showing other whole recording device. 130 in drawing is the recording head of the type which gave the liquid constituent for every color of ink, for example, is the ink jet recording head of 300x600dpi2 trains. 130Y, 130M, 130C, and 130B are the recording heads which made one set one color each and liquid constituent of Y (yellow), M (Magenta), C (cyanogen), and B (black). For example, after printing yellow and a liquid constituent by 130Y, UV lamp of 105 performs UV irradiation and only UV which the front face of ink hardens at least is irradiated.

[0192] By the delivery motor of 111, the recorded media 101 on the conveyance tray 115 are conveyed to the place of the following ink jet recording head of 130M in order to print the following color. An ink front face is stiffened with the UV lamp 105 after printing. Then, a full color image is repeatedly formed with 130C and 130B. Other detailed explanation is the same as explanation of drawing 1 .

[0193] Although drawing 1 and drawing 2 are performing UV irradiation after one color or 4 color printing, they may install a spot UV lamp beside an ink cartridge, and it may carry out UV irradiation for every one pass (un-illustrating).

[Translation done.]

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

EXAMPLE

[Example] Next, an example and the example of a comparison are given and this invention is explained still more concretely. In addition, as long as there is no notice especially, there are mass criteria among a sentence with the "section" and "%."

[0195] First, production of the liquid constituent of this invention is explained. After carrying out the mixed dissolution of each component shown below, pressure filtration was carried out with the membrane filter (a trade name, a FURORO pore filter, Sumitomo Electric Industries make) whose pore size is 1 micrometer, and liquid constituent A-C of this invention was obtained.

[0196] (Synthetic example of hydrated alumina) Aluminum DODEKISHIDO was manufactured by the approach of a publication to U.S. Pat. No. 4,242,271. Next, by the approach indicated by U.S. Pat. No. 4,202,870, said aluminum DODEKISHIDO was hydrolyzed and the alumina slurry was manufactured. Water was added until the solid content of hydrated alumina became 8.2% about this alumina slurry. pH of an alumina slurry was 9.7. Added 3.9% of nitric-acid solution, adjusted pH to 5.3, it was made to ripe at 120 degrees with an autoclave for 7 hours, and the colloidal sol was obtained. The nitric acid adjusted this colloidal sol to pH=4.0, it condensed to 20% of solid content concentration, and the hydrated alumina slurry was produced. A front face is underwater charged in plus and the hydrated alumina in this slurry shows cationicity. Moreover, when made ion exchange water dilute and distribute this hydrated alumina slurry, it was dropped on the collodion membrane, and the test sample was produced and having been observed with the transmission electron microscope, it was the particle of a monotonous configuration.

[0197] <A presentation of the liquid constituent A>, and a glycerol The 10.0 sections and a diethylene glycol The 7.5 sections and a hydrated alumina slurry The 50.0 sections and water After mixing the 32.5 section above-mentioned component for 30 minutes by 3000rpm in an emulsification disperser (TK ROBOMIKKUSU, product made from special opportunity-ized Industry), centrifugal separation processing (for 4000rpm and 15 minutes) was performed, the big and rough particle was removed, and it considered as the liquid constituent A.

[0198]

<液体組成物Bの組成>

- | | |
|---------------------------|-------|
| ・ 1. 5-ペンタンジオール | 10.0部 |
| ・ エチレングリコール | 7.5部 |
| ・ コロイダルジルコニアゾル (固形分濃度20%) | 50.0部 |
| ・ 水 | 32.5部 |

After mixing the above-mentioned component for 30 minutes by 3000rpm in an emulsification disperser (TK ROBOMIKKUSU, product made from special opportunity-ized Industry), centrifugal separation processing (for 4000rpm and 15 minutes) was performed, the big and rough particle was removed, and it considered as the liquid constituent B. A front face is underwater charged in plus and the zirconia particle in this zirconia sol shows cationicity.

[0199] <A presentation of the liquid constituent C>, and a guru serine The 10.0 sections and a diethylene glycol The 7.5 sections and a hydrated alumina slurry The 50.0 sections and a

photopolymerization initiator (IRGACURE 2959, Ciba-Geigy make) The 3.0 sections and water After mixing the 29.5 section above-mentioned component for 30 minutes by 3000rpm in an emulsification disperser (TK ROBOMIKKUSU, product made from special opportunity-ized Industry), centrifugal separation processing (for 4000rpm and 15 minutes) was performed, the big and rough particle was removed, and it considered as the liquid constituent C.

[0200] Above-mentioned liquid constituent A-C was measured by the following approach, and each property and the evaluation result were shown in Table 1.

1) After diluting a liquid constituent with ion exchange water so that it may become 0.1% about the solid content concentration of the mean-particle-diameter particle of a particle, the ultrasonic washing machine was made to distribute for 5 minutes, and dispersion reinforcement was measured using the electrophoresis light scattering photometer (Otsuka Electronic company make, ELS-8000: 25 degrees C of solution temperature, quartz cell use). It asked for mean particle diameter with the KYUMURANTO analysis method from dispersion reinforcement using attached software.

[0201] 2) It measured to pH liquid constituent using the pH meter meter (the Horiba, Ltd. make, caster knee pH meter D-14) at 25 degrees C of solution temperature.

3) After diluting a liquid constituent with ion exchange water so that the solid content concentration of a F-potential particle may become 0.1%, it measured with the F-potential measurement machine (the product made from BURUKKUHEBUN, BI-ZETA plus: 20 degrees C of solution temperature, acrylic cel use).

[0202] 4) After putting a tank shelf-life liquid constituent in an ink tank, standing preservation was carried out for one month at the 60-degree C thermostat, and the liquid nature of the liquid constituent in a tank and the dischargeability from a recording head were evaluated.

O : sedimentation is not mostly seen within a tank but regurgitation stability is also good.

x: Sediment remarkably within a tank and dischargeability is also unstable.

[0203]

表1

液体組成物	A	B	C
平均粒子径 (nm)	70	115	75
pH	4.1	3.9	3.8
ゼータ電位 (mV)	41	69	40
タンク保存性	○	○	○

[0204] Next, production of the ink subsets 1 and 2 used in the example and the example of a comparison of this invention is explained.

Each component shown in the <production of ink subset 1> following was mixed, and it stirred enough, and after the dissolution, pressure filtration was carried out with the FURORO pore filter (a trade name, Sumitomo Electric Industries make) whose pore size is 0.45 micrometers, black, yellow, a Magenta and each color ink of cyanogen, and Bk1, Y1, M1 and C1 were obtained, and combination which consists of these color ink was made into the ink subset 1.

[0205] [Black ink Bk1]

**C. I. direct black 195 The 2.5 sections and 2-pyrrolidone The 10.0 sections and glycerol The 5.0 sections and isopropyl alcohol The 4.0 sections and sodium hydroxide The 0.4 sections and acrylic monomer (*1) The 10.0 sections and water The 68.1 sections [0206] [Yellow ink Y1] - Projet Fast Yellow 2 (product made from Zeneca) The 2.0 sections and C.I. direct yellow 86 The 1.0 sections and thiodiglycol The 8.0 sections and ethylene glycol The 8.0 sections and ASECHIRE Norian EH The 0.2 sections (the Kawaken chemicals company make)

- Isopropyl alcohol The 4.0 sections and acrylic monomer (*1) The 10.0 sections and water The 66.8 sections [0207] [Magenta ink M1]

- Projet Fast Magenta 2 (product made from Zeneca) The 3.0 sections and glycerol The 7.0 sections and urea The 7.0 sections and ASECHIRE Norian EH The 0.2 sections (the Kawaken chemicals company make)

– Isopropyl alcohol The 4.0 sections and acrylic monomer (*1) The 10.0 sections and water The 68.8 sections [0208] [Cyanogen ink C1]

**C. I. direct blue 199 The 3.0 sections and ethylene glycol The 7.0 sections and diethylene glycol The 10.0 sections and ASECHIRE Norian EH The 0.3 sections (the Kawaken chemicals company make)

– Acrylic monomer (*1) The 10.0 sections and water 69.7 section (notes) *1: Ethoxylation trimethylolpropane triacrylate (trade name A-TMPT-3EO, product made from New Nakamura Chemistry)

[0209] By each component shown in the <production of ink subset 2> following, pigment dispersion liquid were prepared and black ink Bk2 was produced using this. Furthermore, yellow, a Magenta and each pigment ink of cyanogen, and Y2, M2 and C2 were obtained using the same pigment dispersion liquid, and combination which consists of these pigment ink was made into the ink subset 2.

[0210] [Black ink Bk2]

(Production of pigment dispersion liquid)

– The styrene-acrylic-acid-ethyl-acrylate copolymer (acid-number 140, weight average molecular weight 5,000) 1.5 section and monoethanolamine The 1.0 sections and diethylene glycol The 5.0 sections and water The 81.5 sections [0211] The above-mentioned component is mixed, it warms at 70 degrees C with a water bath, and a pitch is dissolved completely. After adding the carbon black (MCF88, Mitsubishi Chemical make) 10 section and the isopropyl alcohol 1 section which were newly made by this solution as an experiment and performing pre mixing for 30 minutes, distributed processing was performed on condition that the following.

– Disperser : Sand grinder (product made from the Igarashi machine)

– Grinding media : a zirconium bead, and filling factor:50% of the diameter of 1mm and grinding media (volume ratio)

– Grinding time amount : centrifugal separation processing (for 12,000rpm and 20 minutes) was performed further for 3 hours, the big and rough particle was removed, and it considered as dispersion liquid.

[0212] (Production of black ink Bk2) The above-mentioned pigment dispersion liquid were used, the component which has the following presentation ratio was mixed, the ink containing a pigment was produced, and this was made into black ink Bk2.

– The above-mentioned pigment dispersion liquid The 30.0 sections and glycerol The 10.0 sections and ethylene glycol The 5.0 sections and N-methyl pyrrolidone The 5.0 sections and ethyl alcohol The 2.0 sections and acrylic monomer The 10.0 sections (trade name NK ester A-200, product made from New Nakamura Chemistry)

– Water The 38.0 sections [0213] Pigment content yellow ink Y2 was prepared like preparation of black ink Bk2 except having replaced with the pigment yellow 74 the carbon black (MCF88, Mitsubishi Chemical make) 10 section used on the occasion of preparation of [yellow ink Y2] black ink Bk2.

[0214] Pigment content Magenta ink M2 was prepared like preparation of black ink Bk2 except having replaced with the pigment red 7 the carbon black (MCF88, Mitsubishi Chemical make) 10 mass section used on the occasion of preparation of [Magenta ink M2] black ink Bk2.

[0215] Pigment content cyanogen ink C2 was prepared like preparation of black ink Bk2 except having replaced with the pigment blue 15 the carbon black (MCF88, Mitsubishi Chemical make) 10 mass section used on the occasion of preparation of [cyanogen ink C2] black ink Bk2.

[0216] (An example 1 – example 6) It printed in the combination of the following table 2 using liquid constituent A–C of this invention obtained as mentioned above, and each color ink of the ink subsets 1 and 2. In addition, examples 1–4 performed electron beam irradiation immediately after desiccation for 5 minutes at 60 degrees C after printing. exposure conditions — current: — it carried out by 6mA, and a part for /and line speed:10m dosage:3Mrad. On the other hand, examples 5 and 6 performed UV irradiation immediately after desiccation for 5 minutes at 60 degrees C after printing. The exposure was performed by 10 J/cm². This was made into the examples 1–6 of this invention.

[0217]

表2

実施例	インクサブセット	液体組成物
1	1	A
2	2	A
3	1	B
4	2	B
5	1	C
6	2	C

[0218] In the formation approach of the coloring section of the examples 1-6 used combining liquid constituent A-C and the ink subsets 1 and 2 as mentioned above, it recorded on the PET film of 100-micrometer thickness. Moreover, as an ink JIETO recording device used on that occasion, the color picture was formed using the recording device shown in drawing 1. Under the present circumstances, point-struck the liquid constituent, carried out it, it was made to adhere on a film first, and ink was made to adhere after that. Immediately after printing, energy was given on the above-mentioned conditions, and you stiffened the record image, and made it established. It checked having hardened any example enough.

[0219] Specifically, evaluation-criteria (1) - (5) performed 3 pass fine printing which prints a printing area by three scans. At this time, the liquid constituent printed in the pixel location where the ink of either yellow, a Magenta, cyanogen and black is printed for every pass. That is, the OR of the yellow for every pass, a Magenta, cyanogen, and the printing data of black was used as printing data of a liquid constituent. In addition, there is especially no limit in the class of fine mask at the time of this fine printing, and since the well-known technique is available, detailed explanation here is omitted.

[0220] The recording head used here has the recording density of 600dpi, and made it 9.6kHz of drive frequencies as drive conditions. The discharge quantity per dot when using the head of 600dpi used [constituent / yellow, a Magenta, cyanogen ink, and / liquid] the head of 30ng(s) per dot about 15ng(s) and black ink, respectively. In addition, these record conditions are the same through an example and the example of reference.

[0221] (Examples 1 and 2 of reference) It printed in the combination of the following table 3 only using each color ink of the ink subsets 1 and 2 obtained as mentioned above. In addition, the examples 1 and 2 of reference performed electron beam irradiation immediately after desiccation for 5 minutes at 60 degrees C after printing. exposure conditions — current: — it carried out by 6mA, and a part for /and line speed:10m dosage:3Mrad.

[0222]

表3

参考例	インクサブセット	液体組成物
1	1	なし
2	2	なし

[0223] The recording head used in the record (examples 1-2 of reference) using the above-mentioned liquid constituent C and the ink subsets 1 and 2 has the recording density of 600dpi, and made it 9.6kHz of drive frequencies as drive conditions. The discharge quantity per dot when using the head of 600dpi used [ink / yellow, a Magenta, and / cyanogen] the head of about 30 ng(s) per dot about about 15 ng(s) and black ink, respectively, and recorded on the case of examples 1-6, and these conditions.

[0224] [The evaluation approach and valuation basis] The following evaluation approach and the valuation basis estimated each record image obtained in above-mentioned examples 1-6 and examples 1 and 2 of reference. The result was shown in Table 4.

[0225] (The evaluation approach of a record image)

(1) The RGB color chart of a color-enhancing highly minute XYZ-CIELAB-RGB standard image (SHIPP) (editorial supervision: the highly minute standard image creation committee : Institute of Image Electronics Engineers of Japan issue) was printed using the printer, and the colorimetry of those color charts was carried out. By the approach indicated by this technical explanatory, color-enhancing evaluation calculated three-dimension-breadth (in a sentence, it is hereafter called the color-gamut volume) of color distribution, and compared. At that time, the image processing at the time of forming a printing image was made into the same conditions, and the colorimetry was measured on light source:D50 and visual field:2 degree conditions by GRETAG SUPEKUTORORINO after after [printing] 24-hour progress. The valuation basis was shown below. The ratio of each color-gamut volume of examples 5 and 6 to the examples 1 and 2 over the example 1 of reference, the examples 3 and 4 over the example 2 of reference, and the example 3 of reference was made into the valuation basis.

[0226] AA: A color-gamut volume ratio is 1.4 or more times.

A : a color-gamut volume ratio is less than 1.2 to 1.4 times.

B : a color-gamut volume ratio is less than 1.0 to 1.2 times.

C : a color-gamut volume ratio is less than 1.0 times.

[0227] (2) After printing yellow, a Magenta, cyanogen, and the solid image of black each color using the printer which carried out the homogeneous above, viewing estimated the homogeneity of a color about white MOYA and color nonuniformity. The bad, especially homogeneous color was made applicable to evaluation. The valuation basis is as follows.

A: Hardly generate white MOYA and color nonuniformity.

B: Although white MOYA and color nonuniformity can be seen along with the fiber of paper a little, it is level without a parenchyma top problem.

C: Along with the fiber of paper, white MOYA and color nonuniformity look remarkable.

[0228] (3) After printing yellow, a Magenta, cyanogen, and the solid image of black each color using the printer which carried out the stripe nonuniformity above, viewing estimated stripe nonuniformity. The bad color of especially stripe nonuniformity was made applicable to evaluation. The valuation basis is as follows.

A: Hardly generate stripe nonuniformity.

B: Although the stripe nonuniformity for every head scan can be seen a little, it is level without a parenchyma top problem.

C: The remarkable white stripe nonuniformity for every head scan can be seen.

[0229] (4) Yellow, a Magenta, cyanogen, and the solid image of the ink of black each color were printed using the printer which carried out the scratch-proof nature above. It is JIS about the pencil degree of hardness of the record image 16 hours after printing. It measured according to K5400. What has the lowest degree of hardness was made applicable to evaluation.

[0230] (5) Yellow, a Magenta, cyanogen, and the solid image of the ink of black each color were printed using the printer which carried out the weatherproof above. 24 hours after printing, the ozone weather meter (Suga Test Instruments Co., Ltd. make) performed the record image, and the exposure test was performed whenever [tub internal temperature] on 40 degrees C, 55% of humidity in a tub, the ozone level of 3 ppm, and the conditions of exposure time 2 hours. deltaE of each color before and behind a trial was measured, and the following criteria estimated by making applicable to evaluation what has the most remarkable tint change.

A: Less than deltaE5

B: deltaE5 to less than ten

C: deltaE10 or more

[0231]

表4

	発色性	均一性	スジムラ	耐擦過性	耐候性
実施例1	AA	A	A	4H	A
実施例2	AA	A	A	4H	A
実施例3	A	A	A	4H	A
実施例4	A	A	A	4H	A
実施例5	AA	A	A	4H	A
実施例6	AA	A	A	4H	A
参考例1	B	B	B	4H	A
参考例2	B	B	B	4H	A

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The typical schematic diagram showing the important section of one example of the ink jet recording device of this invention.

[Drawing 2] The typical schematic diagram showing other examples of the ink jet recording device of this invention.

[Drawing 3] The explanatory view showing the example of a configuration of the tray used for the ink jet recording device of this invention.

[Drawing 4] It is drawing showing one example of the location amendment system according to the temperature of the image formation side of the recorded material in the ink jet recording device of this invention, and the recorded material in the case of the alignment of a recording head.

[Drawing 5] The typical sectional view explaining the condition of the coloring section when performing ink jet record to coat paper.

[Drawing 6] The typical sectional view explaining the condition of the coloring section of the ink jet image concerning this invention.

[Drawing 7] The outline process Fig. in which it is shown like the formation fault of the coloring section of the ink jet record image concerning this invention.

[Description of Notations]

101: Recorded media

102: The field where the 1st process is performed

103: The field where the 3rd process is performed

104: UV / O₃ exposure lamp

105: UV irradiation lamp

111 119: Stocker

112: Conveyance machine

118: Handler

113 120: Band conveyor

114: Auxiliary roller

121: Delivery roller

115: The tray for printing

116: Pump

117: Delivery motor

130Y, 130M, 130C, 130B: Each color (Y, M, C, B) and recording head of ink

211: Spacer

401: Recorded media

402: Thermo sensor

403: Motor

410: Recording head

501: Base paper

503: Ink absorbing layer

505: Porosity particle

507: Adhesives
509: Ink osmosis section
601: Recorded media
602: Crosslinked polymer
603: Particle
605: Color material
607: The aggregate of a particle
609: The aggregate of the particle near [in the main image section IM] the recorded-media front face
I: Coloring section
IM: The main image section
IS: The periphery of the main image section
701: The reactant of ink and a liquid constituent
702: Ink which did not participate in a reaction with a liquid constituent
703: Recorded media
704: Color material
705: Monomer
706: Liquid constituent
707: ***** of a liquid constituent
709: The particle near the recorded-media front face
711: The aggregate of a particle
713: Ink
716: External energy given

[Translation done.]

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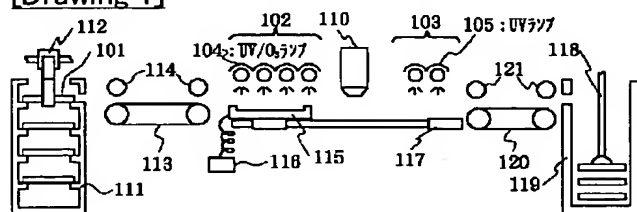
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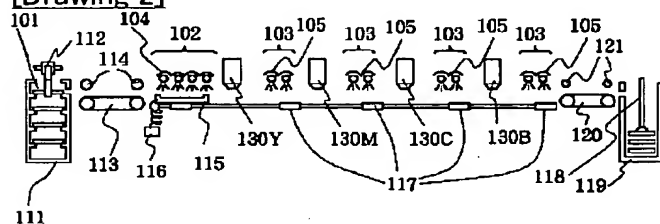
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DRAWINGS

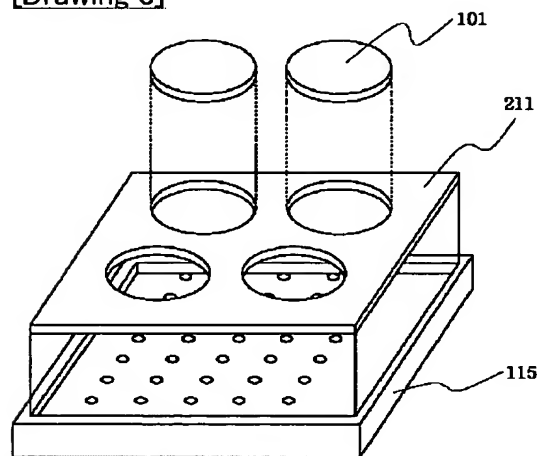
[Drawing 1]



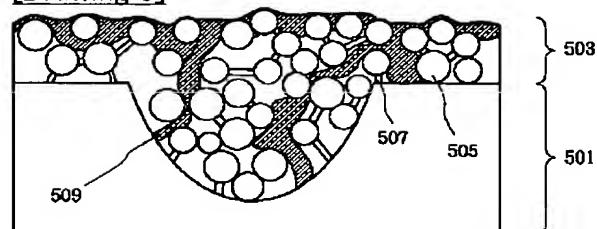
[Drawing 2]



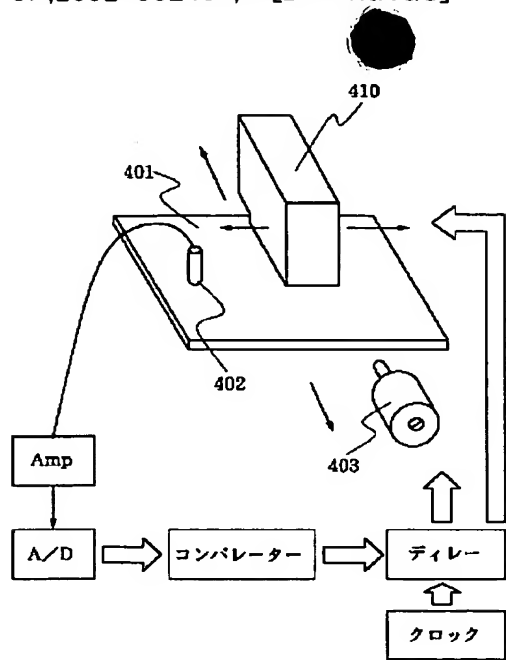
[Drawing 3]



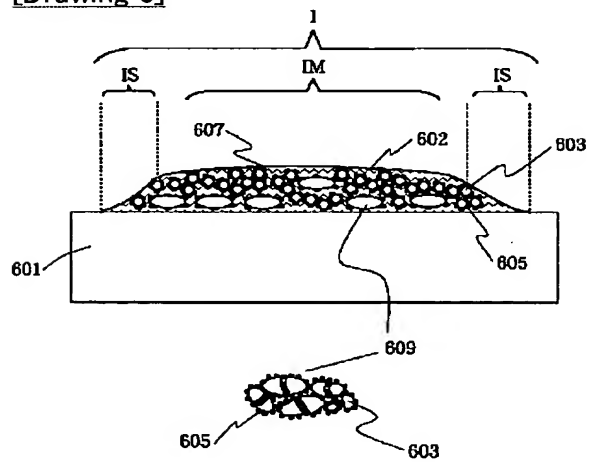
[Drawing 5]



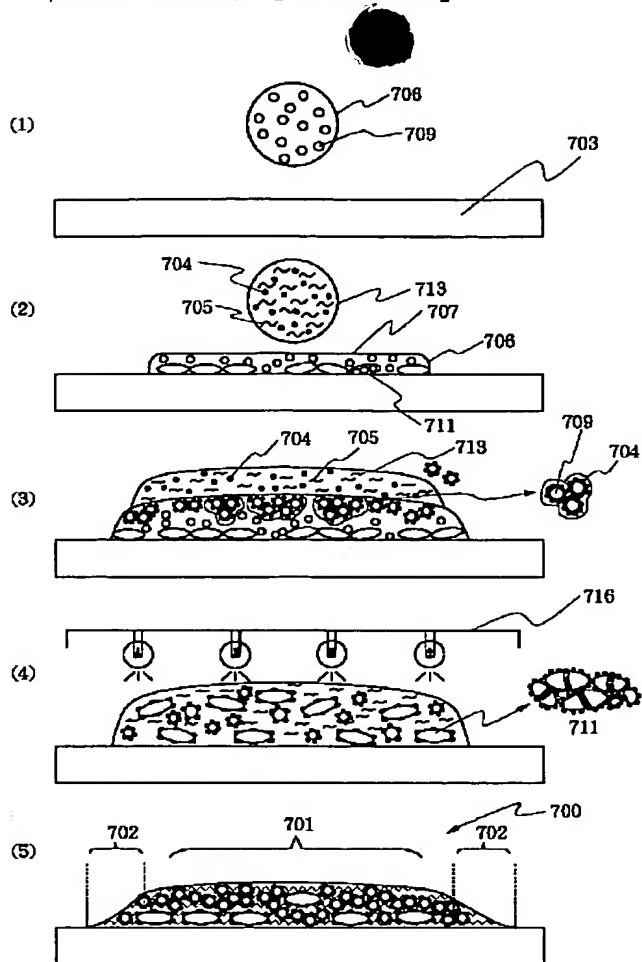
[Drawing 4]



[Drawing 6]



[Drawing 7]



[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2002-332434

(P2002-332434A)

(43) 公開日 平成14年11月22日 (2002. 11. 22)

(51) Int.Cl. ⁷	識別記号	F I	テマコード* (参考)
C 0 9 D 11/00		C 0 9 D 11/00	2 C 0 5 6
B 4 1 J 2/01		B 4 1 M 5/00	A 2 H 0 8 6
B 4 1 M 5/00			E 4 J 0 3 9
		B 4 1 J 3/04	1 0 1 Y
			1 0 1 Z
審査請求 未請求 請求項の数35 O L (全 31 頁)			

(21) 出願番号 特願2001-140535(P2001-140535)

(22) 出願日 平成13年5月10日 (2001. 5. 10)

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最終頁に続く

(54) 【発明の名称】 インクセット、被記録媒体に着色部を形成する方法及びインクジェット記録装置

(57) 【要約】

【課題】 吸液性の乏しい被記録媒体に対して発色性に優れる高品質なインクジェット記録物を得ることができ、信頼性にも優れたインクセット、被記録媒体に着色部を形成する方法及びインクジェット記録装置の提供。

【解決手段】 色材およびエネルギーの付与により重合体に転化するモノマーおよび該モノマーを溶解する溶剤を含むアニオン性若しくはカチオン性の水性インクと、上記インクに対して逆極性に表面が帯電している微粒子を分散状態で含む液体組成物とを組合せたことを特徴とするインクセット、被記録媒体に着色部を形成する方法及びインクジェット記録装置。

【特許請求の範囲】

【請求項 1】 色材とエネルギーの付与により重合体に転化する重合性成分と該重合性成分を溶解する溶剤とを含むアニオン性若しくはカチオン性のインクと、上記インクとは逆極性に表面が帯電している微粒子を分散状態で含む液体組成物とを組み合わせることを特徴とするインクセット。

【請求項 2】 付与するエネルギーが紫外線、電子線、又は熱である請求項 1 に記載のインクセット。

【請求項 3】 更に光重合開始剤を液体組成物及び／又はインクに含む請求項 1 に記載のインクセット。

【請求項 4】 微粒子が、被記録媒体上に着色部を形成する際に、インク中の色材の凝集を防ぎつつ、該微粒子表面に色材が吸着されるように構成されている請求項 1 に記載のインクセット。

【請求項 5】 微粒子が、被記録媒体上に着色部を形成する際に、その表面にインク中の色材が単分子状態で吸着されるように構成されている請求項 1 に記載のインクセット。

【請求項 6】 インクが、イエローインク、マゼンタインク、シアンインク、ブラックインク、レッドインク、ブルーインク及びグリーンインクから選ばれる少なくとも 1 つである請求項 1 に記載のインクセット。

【請求項 7】 インクが、イエローインク、マゼンタインク及びシアンインクを各々別個の状態を含んでいる請求項 1 に記載のインクセット。

【請求項 8】 インクが、イエローインク、マゼンタインク、シアンインク及びブラックインクを各々別個の状態を含んでいる請求項 1 に記載のインクセット。

【請求項 9】 インクがアニオン性であり、且つ液体組成物のゼータ電位が $+5 \sim +90$ mV の範囲にある請求項 1 に記載のインクセット。

【請求項 10】 インクがアニオン性であり、且つ液体組成物が酸を含み、該液体組成物の pH が $2 \sim 7$ に調整されている請求項 1 に記載のインクセット。

【請求項 11】 酸の水中での一次解離定数 pK_a が 5 以下である請求項 10 に記載のインクセット。

【請求項 12】 インクがアニオン性を有し、且つインクにアニオン性化合物が含有されている請求項 1 ～ 11 のいずれか 1 項に記載のインクセット。

【請求項 13】 アニオン性化合物としてアニオン性基を有する水溶性染料を含む請求項 12 に記載のインクセット。

【請求項 14】 アニオン性化合物として表面にアニオン性基を有する顔料を含む請求項 12 に記載のインクセット。

【請求項 15】 インクが、顔料と、該顔料の分散剤であるアニオン性化合物とを含む請求項 12 に記載のインクセット。

【請求項 16】 インクがカチオン性であり、且つ液体

組成物のゼータ電位が $-5 \sim -90$ mV の範囲にある請求項 1 に記載のインクセット。

【請求項 17】 インクがカチオン性であり、且つ液体組成物が塩基を含み、該液体組成物の pH が $7 \sim 12$ の範囲に調整されている請求項 1 に記載のインクセット。

【請求項 18】 塩基の水中での一次解離定数 pK_b が 5 以下である請求項 17 に記載のインクセット。

【請求項 19】 インクがカチオン性を有し、且つ該インクにカチオン性化合物が含有されている請求項 1 ～ 8 及び請求項 16 ～ 18 のいずれか 1 項に記載のインクセット。

【請求項 20】 微粒子の平均粒子直径が $0.005 \sim 1$ μ m の範囲にある請求項 1 ～ 19 のいずれか 1 項に記載のインクセット。

【請求項 21】 (i) 色材とエネルギーの付与により重合する重合性成分と該重合性成分を溶解する溶剤とを含むアニオン性若しくはカチオン性のインクを被記録媒体に付与する過程、及び (ii) 該インクとは逆の極性に表面が帯電している微粒子を分散状態で含む液体組成物を被記録媒体に付与する過程を有する被記録媒体に着色部を形成する方法であって、上記被記録媒体の表面に、上記インクと液体組成物とが互いに液体状態で接するように付与されることを特徴とする被記録媒体への着色部の形成方法。

【請求項 22】 少なくとも過程 (ii) が行われた後に、過程 (i) が行われる請求項 21 に記載の被記録媒体への着色部の形成方法。

【請求項 23】 少なくとも過程 (i) が行われた後に、過程 (ii) が行われる請求項 21 に記載の被記録媒体への着色部の形成方法。

【請求項 24】 過程 (i) が行われた後に、過程 (i) が行われ、その後に再び過程 (i) が行われるように構成する請求項 21 に記載の被記録媒体への着色部の形成方法。

【請求項 25】 過程 (i) におけるインクの被記録媒体への付与を、該インクを記録信号に応じてオリフィスから吐出させる方式のインクジェット記録方法によって行なう請求項 21 ～ 24 のいずれか 1 項に記載の被記録媒体への着色部の形成方法。

【請求項 26】 インクジェット記録方法が、インクに熱エネルギーを作用させることによってインクをオリフィスから吐出させる方法である請求項 25 に記載の被記録媒体への着色部の形成方法。

【請求項 27】 過程 (ii) における液体組成物の被記録媒体への付与を、該液体組成物を記録信号に応じてオリフィスから吐出させる方式のインクジェット記録方法によって行なう請求項 21 ～ 26 のいずれか 1 項に記載の被記録媒体への着色部の形成方法。

【請求項 28】 インクジェット記録方法が、液体組成物に熱エネルギーを作用させて液体組成物をオリフィス

から吐出させる方法である請求項 27 に記載の被記録媒体への着色部の形成方法。

【請求項 29】 請求項 21～28 のいずれか 1 項に記載の方法により着色部を形成した後、エネルギーを付与して該重合性成分を重合する過程を行うことを特徴とする被記録媒体への着色部の形成方法。

【請求項 30】 付与するエネルギーが紫外線、電子線、又は熱である請求項 29 に記載の被記録媒体への着色部の形成方法。

【請求項 31】 色材とエネルギーの付与により重合する重合性成分と該重合性成分を溶解する溶剤とを含むアニオン性若しくはカチオン性のインクを収容したインク収容部と、該インクを吐出させるためのインクジェットヘッドを備えた第 1 の記録ユニットと、上記インクとは逆の極性に表面が帯電している微粒子を分散状態で含む液体組成物を収容した液体組成物収容部と、該液体組成物を吐出させるためのインクジェットヘッドとを備えた第 2 の記録ユニットと、該重合性成分を重合する手段とを備えていることを特徴とするインクジェット記録装置。

【請求項 32】 色材とエネルギーの付与により重合体に転化する重合性成分と該重合性成分を溶解する溶剤とを含むアニオン性若しくはカチオン性のインクを収容したインク収容部と、該インクとは逆の極性に表面が帯電している微粒子を分散状態で含む液体組成物を収容した液体組成物収容部と、上記インク収容部に収容されているインクと上記液体組成物収容部に収容されている液体組成物とを各々独立に吐出させるためのインクジェットヘッドと、該重合性成分を重合する手段とを備えていることを特徴とするインクジェット記録装置。

【請求項 33】 インクジェットヘッドが、熱エネルギーを作用させて液体を吐出させるサーマルインクジェットヘッドである請求項 31 又は 32 に記載のインクジェット記録装置。

【請求項 34】 付与するエネルギーが紫外線、電子線、又は熱である請求項 29 に記載の被記録媒体への着色部の形成方法。

【請求項 35】 色材とエネルギーの付与により重合する重合性成分と該重合性成分を溶解する溶剤とを含むアニオン性又はカチオン性のインクとともに被記録媒体に付与され、該被記録媒体上に着色部を形成するのに用いられる微粒子を含む液体組成物であって、上記着色部の形成が、上記液体組成物と上記インクとが液体の状態で接触し、且つ液体組成物の微粒子表面に、インク中の色材がインク中で有している分子状態と実質的に同等の分子状態を保持しつつ吸着若しくは結合してなされることを特徴とする液体組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、カラー画像の形成

において発色性と色の均一性に優れた画像を得る技術に関し、とりわけ、インクジェット記録方式を利用して印刷用のアート紙やプラスチック、金属等の吸液性の乏しい被記録媒体への画像形成に最適に使用できる液体組成物及びこれを用いたインクセット、被記録媒体に着色部を形成する方法及びインクジェット記録装置に関する。

【0002】

【従来の技術】 インクジェット記録方法は、インクを飛翔させ、紙等の被記録媒体にインクを付着させて記録を行うものである。例えば、特公昭 61-59911 号公報、特公昭 61-59912 号公報及び特公昭 61-59914 号公報において開示されている、吐出エネルギー供給手段として電気変換体を用い、熱エネルギーをインクに与えて気泡を発生させることにより液滴を吐出させる方式のインクジェット記録方法によれば、記録ヘッドの高密度マルチオリフィス化を容易に実現することができ、高解像度及び高品位の画像を高速で記録することができる。

【0003】 ところで、従来のインクジェット記録方法に用いられるインクは、水を主成分とし、これにノズル内でのインクの乾燥防止、ノズルの目詰まり防止等の目的でグリコール等の水溶性高沸点溶剤を含有しているものが一般的である。そのためこのようなインクを用いて被記録媒体に記録を行った場合には、十分な定着性が得られなかったり、被記録媒体としての記録紙表面における填料やサイズ剤の不均一な分布によると推定される不均一画像の発生等の問題を生じる場合がある。

【0004】 一方、近年は、インクジェット記録物に対しても、銀塩写真と同レベルの高い画質を求める要求が強くなっており、インクジェット記録画像の画像濃度を高めること、色再現領域を広げること、更には記録物の色の均一性を向上させることに対する技術的な要求が非常に高くなっている。

【0005】 このような状況のもとで、インクジェット記録方法の安定化、そしてインクジェット記録方法による記録物の品質向上を図るために、これまでに種々の提案がなされてきている。被記録媒体に関する提案のうちの 1 つとして、被記録媒体の基紙表面に、充填材やサイズ剤を塗工する方法が提案されており、例えば、充填材として色材を吸着する多孔質微粒子を基紙に塗工し、この多孔質微粒子によってインク受容層を形成する技術が開示されている。これらの技術を用いた被記録媒体として、インクジェット用コート紙等が発売されている。

【0006】 このような状況のもとで、インクジェット記録方法の安定化、そしてインクジェット記録方法による記録物の品質向上を図るために、これまでに種々の提案がなされてきている。以下に、その代表的なものの幾つかをまとめる。

(1) インクに揮発性溶剤や浸透溶剤を内添する方法：被記録媒体へのインクの定着性を早める手段として特開

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昭 55-65269 号公報に、インク中に界面活性剤等の浸透性を高める化合物を添加する方法が開示されている。また、特開昭 55-66976 号公報には、揮発性溶剤を主体としたインクを用いることが開示されている。

(2) インクに、インクと反応する液体組成物を被記録媒体上で混合する方法：画像濃度の向上、耐水性の向上、更にはブリーディングの抑制を目的として、記録画像を形成するためのインクの噴射に先立ち或いは噴射後に、被記録媒体上に画像を良好にせしめる液体組成物を付与する方法が提案されている。

【0007】例えば、特開昭 63-60783 号公報には、塩基性ポリマーを含有する液体組成物を被記録媒体に付着させた後、アニオン染料を含有したインクによって記録する方法が開示されており、特開昭 63-22681 号公報には、反応性化学種を含む第 1 の液体組成物と該反応性化学種と反応を起こす化合物を含む第二の液体組成物を被記録媒体上で混合する記録方法が開示されており、更に特開昭 63-299971 号公報には、1 分子当たり 2 個以上のカチオン性基を有する有機化合物を含有する液体組成物を被記録媒体上に付与した後、アニオン染料を含有するインクで記録する方法が開示されている。また、特開昭 64-9279 号公報には、コハク酸等を含有した酸性液体組成物を被記録媒体上に付与した後、アニオン染料を含有したインクで記録する方法が開示されている。

【0008】また、更に特開昭 64-63185 号公報には、染料を不溶化させる液体組成物をインクの付与に先立って紙に付与するという方法が、特開平 8-224955 号公報には、分子量分布領域の異なるカチオン性物質を含む液体組成物を、アニオン性化合物を含むインクとともに用いる方法が開示され、特開平 8-72393 号公報には、カチオン性物質と微粉碎セルロースを含む液体組成物をインクとともに用いる方法がそれぞれ開示されている。

【0009】これらの公開公報には、いずれも画像濃度が高く、印字品位、耐水性が良好で、色再現性、ブリーディングにおいても良好な画像が得られることが記載されている。更に、特開昭 55-150396 号公報には、被記録媒体上に染料インクで記録した後、染料とレーキを形成する耐水化剤を付与する方法が開示され、記録画像の耐水性を付与することが提案されている。

【0010】(3) インクと微粒子含有液体組成物とを被記録媒体上で混合する方法：特開平 4-259590 号公報には、無機物質からなる無色の微粒子を含有する無色液体を被記録媒体上に付与した後、非水系記録液を付着させる方法が開示され、特開平 6-92010 号公報には、微粒子を含む溶液、又は微粒子及びバインダーポリマーを含む溶液を被記録媒体上に付与した後、顔料、水溶性樹脂、水溶性溶剤及び水を含むインクを付着

させる方法が開示され、特開 2000-34432 号公報には水不溶性微粒子から成る液体組成物とインクとを含む記録材料が開示されており、いずれも、紙種によらず印字品位や発色性の良好な画像が得られることが記載されている。

【0011】また、一方で従来、吸液性に乏しい基材に対して画像形成する方法として常温で固化するワックス系組成物に染料を溶解し、加熱溶融した状態でヘッドより噴射し印字するソリッドインク等が知られている。更にはプラスチック基板への画像形成方法として、紫外線硬化型樹脂を用いたものが、特開昭 63-235382 号公報、特開平 3-43292 号公報、特公昭 60-27589 号公報、特公平 5-64667 号公報、特開平 5-186725 号公報、特開平 7-224241 号公報、特開平 8-150707 号公報、特開平 8-218018 号公報等が開示されている。

【0012】(背景技術) 本発明者らは上記したような各種のインクジェット記録技術について検討を重ねた結果、各々の技術課題に対しては優れた効果を確認できるものの、それと引き換えに、他のインクジェット記録特性が低下してしまう場合があることを見出した。例えば、上記した被記録媒体の基紙表面に充填材やサイズ剤を塗工して得られる被記録媒体（以降コート紙という）は、高品質な画像を形成することができる技術として認知されている。

【0013】一般に、高彩度の画像を得るためには、色材を凝集させずに単分子状態で被記録媒体の表面に残すことが必要であることは知られている。コート紙の多孔質微粒子には、このような機能がある。しかしながら、高い画像濃度と画像彩度を得るためには、与えられたインク中の色材に対して、多量の多孔質微粒子で、基紙を覆い隠すような厚いインク受容層の形成が不可欠となり、結果として、基紙の質感が失われてしまうという問題がある。本発明者らは、このように基紙の質感を失う程のインク受容層が必要なのは、色材が、多孔質微粒子に効率的に吸着していないことに起因すると推測した。

【0014】一層のインク受容層を有するコート紙を想定して、以下に従来のコート紙について説明する。図 5 は、コート紙表面付近の断面を模式的に示したものである。同図において、501 は基紙であり、503 はインク受容層を示す。一般に、インク受容層 503 は、多孔質微粒子 505 とそれらを固定化する接着剤 507 を有する。インクが付与されると、インクは多孔質微粒子 505 間の空隙を毛管現象によって浸透し、インク浸透部 505 を形成する。同図に示した様にインク受容層での多孔質微粒子は局所的には密度が異なるため、この毛管現象によるインクの浸透の仕方は場所によって異なる。このため、インクの浸透過程において、色材は多孔質微粒子表面に均一には接触できず、色材が効率的に多孔質微粒子に吸着されない。

【0015】更に接着剤507によってインクの浸透が阻害される部分も生じており、インク受容層503内にはインクが浸透できない部分が存在し、発色には寄与しない部分が発生する。即ち、従来のコート紙においては、上記のような理由により、多孔質微粒子の量に対して効率的に色材を単分子状態で吸着することができず、この結果、高品質の画像を得るためには多量の多孔質微粒子が必要となり、基紙の質感を損なうこととなっていた。

【0016】また、上記(1)の技術を採用することで、インクの被記録媒体への定着性は向上するものの、画像濃度の低下や、普通紙への記録やカラー画像の記録に重要とされる色再現範囲が低下してしまう場合があった。また、上記(2)の技術によれば、インク中の色材を被記録媒体表面に留めることができるため、高い画像濃度の記録物を得ることができる。しかし、色材を被記録媒体の表面で凝集させているためか、色の再現範囲や彩度が十分に得られない場合があった。また、上記

(3)で説明した従来技術では、微粒子を含む溶液の付与により被記録媒体の表面状態の改質は得られたものの、コート紙と同等レベルの高精細な画像は得られなかった。特に、非水系記録液に関しては色材の選択性や記録付与方法等の制限もあり、その自由度に課題が残る。

【0017】また、被記録媒体がコート紙のようなインク受容層等の表面処理を施していない様な、吸液性の乏しい印刷用のアート紙やプラスチック、金属等の材質である場合に対しては以下のような問題があった。

1. 水系インクは紙への溶剤浸透性を利用しており、被記録材としてプラスチック等を用いる場合、インクの乾燥までに時間がかかると同時に耐摩耗性のある画像を形成することができない。従って、被記録媒体としては、紙のような吸収性のあるものやプラスチック等の基材上にインク受容層を設けた被記録媒体が対象になる。また、特開平8-150707号公報ではあらかじめインク浸透性や付着性のある液体をインクジェットにて画像形成部に記録し受容層を形成している。しかし、この方法では前述のコート紙のように厚い受容層を形成する必要が生じ、十分な発色性を有する画像を得るために受容層塗布液が大量に必要となる問題がある。また、着色部の強度も十分に得られないことがあった。

【0018】2. ソリッドインクでは、被記録媒体は特に制限されないで適用できるが、ワックスという柔らかい材質であるために弱い摩擦力でも容易に印字ドットが剥れてしまう。

3. 色材として、昇華性染料を用いた特公昭60-27589号公報のインクに関しては、被記録媒体を120℃～180℃に加熱する必要があるが、被記録媒体が制限される。

4. これまでに開示されてきた色材及び紫外線硬化型樹脂との組み合わせによるインクジェット記録方法ではプ

ラスチック等の基材上で耐候性や耐擦過性に優れた画像形成を可能にしていたが、近年のインクジェット記録用フォトペーパーやフォトフィルム等の被記録媒体と比較して記録画像の発色性やキレ等は十分なものではなかった。

【0019】

【発明が解決しようとする課題】このように、従来の方法にはいずれも課題が残されているため、近年において求められているより一層の高品位なインクジェット記録物に対しては、新たなインクジェット記録技術の開発が必要であるとの認識を、本発明者らは持つに至った。本発明は、上記した新たな知見に基づき為されたものである。即ち、本発明者らは、以上のような新たな知見に基づき、色材を吸着する作用を有する微粒子を用い、且つ該微粒子に効率的に色材を吸着若しくは結合させるために、該微粒子を分散させ、インクとともに液体状態で用いることにより、色材と微粒子とを液-液状態で反応させることが可能となり、その結果として画像の濃度や彩度、耐候性、耐擦過性を信頼性良く向上させることができることを見出し、本発明を為すに至った。

【0020】(本発明の目的)従って本発明の目的は、より一層広い色再現範囲を有し、色の均一性にも優れた高品質なインクジェット記録物を、吸液性の乏しい被記録媒体上において得るために用いられる液体組成物を提供するとともに、耐候性や耐擦過性に優れた記録物を与え、印字における信頼性、具体的には保存安定性、記録ヘッドからの吐出安定性にも優れる液体組成物を提供することにある。

【0021】また、本発明の他の目的は、より一層広い色再現範囲を有し、色の均一性にも優れ、更にベタ部のスジムラが少なく、良好な耐候性や耐擦過性をも備えた優れたインクジェット記録物を吸液性の乏しい被記録媒体上において形成するとともに、被記録媒体に印字における信頼性にも優れる着色部を形成する方法を提供する点にある。

【0022】また、本発明の他の目的は、より一層色再現範囲が広く、色の均一性にも優れ、ベタ部のスジムラの発生が良好な状態に抑制された耐候性や耐擦過性にも優れたインクジェット記録物を吸液性の乏しい被記録媒体上において形成するとともに、印字における信頼性にも優れる液体組成物、該液体組成物を組み合わせたインクセット、インクジェット記録装置を提供することにある。

【0023】

【課題を解決するための手段】上記目的は、下記の本発明によって達成することができる。即ち、本発明は、色材とエネルギーの付与により重合体に転化する重合性成分と該重合性成分を溶解する溶剤とを含むアニオン性若しくはカチオン性のインクと、上記インクとは逆極性に表面が帯電している微粒子を分散状態で含む液体組成物

とを組み合わせたことを特徴とするインクセットを提供する。

【0024】また、本発明は、付与するエネルギーが紫外線、電子線、又は熱である上記のインクセット；更に光重合開始剤を液体組成物及び／又はインクに含む上記のインクセット；微粒子が、被記録媒体上に着色部を形成する際に、インク中の色材の凝集を防ぎつつ、該微粒子表面に色材が吸着されるように構成されている上記のインクセット；微粒子が、被記録媒体上に着色部を形成する際に、その表面にインク中の色材が単分子状態で吸着されるように構成されている上記のインクセット；インクが、イエローインク、マゼンタインク、シアンインク、ブラックインク、レッドインク、ブルーインク及びグリーンインクから選ばれる少なくとも1つである上記のインクセット；インクが、イエローインク、マゼンタインク及びシアンインクを各々別個の状態で含んでいる上記のインクセット；インクが、イエローインク、マゼンタインク、シアンインク及びブラックインクを各々別個の状態で含んでいる上記のインクセットを提供する。

【0025】また、本発明は、インクがアニオン性であり、且つ液体組成物のゼータ電位が $+5 \sim +90 \text{ mV}$ の範囲にある上記のインクセット；インクがアニオン性であり、且つ液体組成物が酸を含み、該液体組成物の pH が $2 \sim 7$ に調整されている上記のインクセット；酸の水溶液中での一次解離定数 pK_a が5以下である上記のインクセット；インクがアニオン性を有し、且つインクにアニオン性化合物が含有されている上記のインクセット；アニオン性化合物としてアニオン性基を有する水溶性染料を含む上記のインクセット；アニオン性化合物として表面にアニオン性基を有する顔料を含む上記のインクセット；インクが、顔料と、該顔料の分散剤であるアニオン性化合物とを含む上記のインクセット；インクがカチオン性であり、且つ液体組成物のゼータ電位が $-5 \sim -90 \text{ mV}$ の範囲にある上記のインクセット；インクがカチオン性であり、且つ液体組成物が塩基を含み、該液体組成物の pH が $7 \sim 12$ の範囲に調整されている上記のインクセット；塩基の水溶液中での一次解離定数 pK_b が5以下である上記のインクセット；インクがカチオン性を有し、且つ該インクにカチオン性化合物が含有されている上記のインクセット；微粒子の平均粒子直径が $0.005 \sim 1 \mu\text{m}$ の範囲にある上記のインクセットを提供する。

【0026】また、本発明は、(i) 色材とエネルギーの付与により重合する重合性成分と該重合性成分を溶解する溶剤とを含むアニオン性若しくはカチオン性のインクを被記録媒体に付与する過程、及び(ii) 該インクとは逆の極性に表面が帯電している微粒子を分散状態で含む液体組成物を被記録媒体に付与する過程を有する被記録媒体に着色部を形成する方法であって、上記被記録媒体の表面に、上記インクと液体組成物とが互いに液体状

態で接するように付与されることを特徴とする被記録媒体への着色部の形成方法を提供する。

【0027】また、本発明は、少なくとも過程(ii)が行われた後に、過程(i)が行われる上記の着色部の形成方法；少なくとも過程(i)が行われた後に、過程(ii)が行われる上記の着色部の形成方法；過程(i)が行われた後に、過程(ii)が行われ、その後に再び過程(i)が行われるように構成する上記の着色部の形成方法；過程(i)におけるインクの被記録媒体への付与を、該インクを記録信号に応じてオリフィスから吐出させる方式のインクジェット記録方法によって行なう上記の着色部の形成方法；インクジェット記録方法が、インクに熱エネルギーを作用させることによってインクをオリフィスから吐出させる方法である上記の着色部の形成方法；過程(ii)における液体組成物の被記録媒体への付与を、該液体組成物を記録信号に応じてオリフィスから吐出させる方式のインクジェット記録方法によって行なう上記の着色部の形成方法；インクジェット記録方法が、液体組成物に熱エネルギーを作用させて液体組成物をオリフィスから吐出させる方法である上記の着色部の形成方法；以上の方法により着色部を形成した後、エネルギーを付与して該重合性成分を重合する過程を行う上記の着色部の形成方法；付与するエネルギーが紫外線、電子線、又は熱である上記の着色部の形成方法を提供する。

【0028】また、本発明は、色材とエネルギーの付与により重合する重合性成分と該重合性成分を溶解する溶剤とを含むアニオン性若しくはカチオン性のインクを収容したインク収容部と、該インクを吐出させるためのインクジェットヘッドを備えた第1の記録ユニットと、上記インクとは逆の極性に表面が帯電している微粒子を分散状態で含む液体組成物を収容した液体組成物収容部と、該液体組成物を吐出させるためのインクジェットヘッドとを備えた第2の記録ユニットと、該重合性成分を重合する手段とを備えていることを特徴とするインクジェット記録装置を提供する。

【0029】また、本発明は、色材とエネルギーの付与により重合体に転化する重合性成分と該重合性成分を溶解する溶剤とを含むアニオン性若しくはカチオン性のインクを収容したインク収容部と、該インクとは逆の極性に表面が帯電している微粒子を分散状態で含む液体組成物を収容した液体組成物収容部と、上記インク収容部に収容されているインクと上記液体組成物収容部に収容されている液体組成物とを各々独立に吐出させるためのインクジェットヘッドと、該重合性成分を重合する手段とを備えていることを特徴とするインクジェット記録装置；インクジェットヘッドが、熱エネルギーを作用させて液体を吐出させるサーマルインクジェットヘッドである上記のインクジェット記録装置；付与するエネルギーが紫外線、電子線、又は熱である上記のインクジェット

記録装置を提供する。

【0030】また、本発明は、色材とエネルギーの付与により重合する重合性成分と該重合性成分を溶解する溶剤とを含むアニオン性又はカチオン性のインクとともに被記録媒体に付与され、該被記録媒体上に着色部を形成するのに用いられる微粒子を含む液体組成物であって、上記着色部の形成が、上記液体組成物と上記インクとが液体の状態で接触し、且つ液体組成物の微粒子表面に、インク中の色材がインク中で有している分子状態と実質的に同等の分子状態を保持しつつ吸着若しくは結合してなされることを特徴とする液体組成物を提供する。

【0031】

【発明の実施の形態】次に、好ましい実施の形態を挙げて本発明を更に詳しく説明する。本発明の被記録媒体に着色部を形成する方法の好ましい実施態様としては、

(i) 上記本発明の色材等を含むインクを被記録媒体に付与する過程、及び(ii) 上記本発明の液体組成物を被記録媒体に付与する過程とを有し、且つ上記被記録媒体の表面に、インクと液体組成物とが互いに液体状態で接するように付与されるように構成し、且つ着色部を形成した後、エネルギーを付与して重合性成分（以下ではモノマーと称することがある）を重合体に転化する態様が挙げられる。かかる実施態様を採用することによって、より一層広い色再現領域を有し、色の均一性にも優れ、更にベタ部のスジムラが少なく、良好な耐候性や耐擦過性をも備えたインクジェット記録物が吸液性の乏しい被記録媒体上において安定して得られる。また、記録に用いるインクや液体組成物自体は、上記したように、その構成が極めてシンプルであるために、高品質且つ高信頼性のインクジェット記録を行なうことができるという効果が得られる。

【0032】（メカニズムの説明）本発明によって上記したような優れた効果が奏される理由は明らかでないが、本発明者らは、以下の理由によるものと考えている。まず、本発明における記録のメカニズムについて、図6及び図7に従って説明する。尚、ここでは、インクとしてアニオン性基を有する水溶性染料（アニオン性染料）とエネルギー付与によって重合体に転化する重合性成分（モノマー）を含む水性インクを用い、同時に液体組成物として、表面がカチオン性に帯電している微粒子を分散状態で含んでいる水性の液体組成物を用い、被記録媒体として吸液性の極めて乏しいプラスチックを用いた場合について説明する。

【0033】以下に、本発明にかかる記録画像について図6を用いて説明する。まず、説明に先立ち言葉の定義を行う。本発明において「単分子状態」とは、染料や顔料等の色材が、インク中で溶解若しくは分散した状態をほぼ保っていることを指している。このとき、色材が多少の凝集を引き起こしたとしても、彩度が低下しない範囲であれば、この「単分子状態」に含まれることとす

る。例えば、染料の場合、単分子であることが好ましいと考えられるため、便宜上染料以外の色材についても「単分子状態」と呼ぶこととする。また、本発明において「色材と微粒子との反応」とは、両者の共有結合の他、イオンの結合、物理的・化学的吸着、吸収、付着、その他の両者の相互作用を意味するものとする。

【0034】図6は、本発明にかかる記録画像の着色部Iが、主画像部IMとその周辺部ISとから成り立っている状態を模式的に示した図である。図6において、601は被記録媒体、603は、色材605が化学的に吸着する微粒子を模式的に示したものである。図6に示したように、本発明のインクジェット記録画像では、主画像部IMは、色材605が、単分子或いは単分子に近い状態（以降「単分子状態」と略す）で均一に表面に吸着した微粒子603と、色材の単分子状態を保持した微粒子の凝集物607とモノマーにエネルギーが付与され、重合及び架橋して形成された三次元架橋ポリマー602で構成されている。

【0035】609は、主画像部IM内の被記録媒体表面近傍に存在する、微粒子同士の凝集物である。主画像部IMは、被記録媒体表面に微粒子603が物理的又は化学的に吸着する過程と、色材605と微粒子603とが液-液状態で吸着する過程、モノマーがエネルギー付与によって転化した三次元架橋ポリマーで着色部I全体を固化及び被記録媒体に密着する過程とによって形成されたものである。そのため、色材自体の発色特性が損なわれることが少なく、プラスチックや金属等吸液性の乏しい記録媒体においても、画像濃度や彩度が高く、コート紙並みに色再現範囲の広く、耐候性や耐擦過性に優れた画像形成が可能となる。一方、微粒子表面603に吸着されず、インク中に残った色材605は、被記録媒体601に対して横方向に拡散するため、周辺部ISに色材605とモノマーが転化した三次元架橋ポリマー602により微少な滲みを形成する。このように記録媒体601の表面近傍に色材が残り、且つ周辺部にインクの微少な滲みを形成させるために、シャドウ部やベタ部等のインク付与量が多い画像領域においても、白モヤや色ムラが少なく色の均一性に優れる。

【0036】更に本発明の液体組成物を用いた場合においては、被記録媒体の表面近傍に存在する微粒子凝集物609が形成される際に、凝集物の内部にある程度の大きさの細孔が形成される。前述のインク中で単独に存在していた色材605は微粒子凝集物609の細孔内部へと浸透し、細孔の入口付近や内壁に理想的な単分子状態で吸着して、色材をより多く理想的な状態で被記録媒体の表面近傍に残留させることができる。これによってより一層優れた発色性の記録物を得ることができる。

【0037】図7(1)～(5)は、本発明にかかる被記録媒体に着色部を形成する方法の1実施態様の着色部700の概略断面図及びその形成過程を説明する概略過

程図である。図 7 において、701 はインクと液体組成物との反応物、例えば、色材と微粒子との反応物を主として含む部分（以降「反応部」と略す）であり、図 6 の主画像部 IM に相当する部分である。702 は、液体組成物中の微粒子との反応に実質的に関与しなかったインクが、反応部 701 の辺縁に流出することによって形成された部分（以降「インク流出部」と略す）であり、図 6 の周辺部 IS に相当する。かかる着色部 700 は、例えば、以下のようにして形成される。

【0038】 先ず、インク中の色材 704 と反応性を有する液体組成物 706 とが液滴として被記録媒体 703 に付与され（図 7（1））、その結果、液体組成物の液溜り 707 が形成される（図 7（2））。該液溜り 707 内で、被記録媒体表面近傍の微粒子 709 は、被記録媒体の表面に物理的又は化学的に吸着する。この時、分散状態が不安定となって微粒子同士の凝集物 711 を形成するものもあると考えられる。一方で、液溜り 707 内の被記録媒体との界面より離れた部分では、微粒子 709 はもとの分散状態を保っていると考えられる。

【0039】 次いで、インク 713 が液滴として被記録媒体 703 に付与される（図 7（2））。その結果、先ずインク 713 と液溜り 707 の界面において色材 704 は、微粒子 709 に化学的に吸着する。この反応は、液同士の反応（液-液反応）であるため、色材 704 は単分子状態で、微粒子 709 の表面に均一に吸着すると考えられる。即ち、微粒子表面では、色材同士は凝集を起こさないか、或いは凝集しても僅かであると推測される。その結果、反応部 701 の表層部に単分子状態で色材 704 が吸着された微粒子が多数形成され、発色に最も影響を与える着色部に色材を単分子状態で残存させることができるため、高画像濃度であって、且つ彩度の高い記録画像を形成する。

【0040】 次いで、これら色材 704 が吸着した微粒子は、分散状態が不安定となるため微粒子同士で凝集すると考えられる。即ち、ここで形成された凝集物 715 は、その内部にも単分子状態の色材を保持している。この凝集物 715 により高画像濃度且つ高彩度の記録画像が形成される。

【0041】 更に未反応の色材 704 の一部は、液溜り 707 内を拡散し、未反応の微粒子 709 の表面に吸着する。このように、液溜り 707 内部で色材と微粒子との反応が更に進行するため、より高濃度で彩度の高い画像が形成される。そして被記録媒体 703 は吸液性が極めて乏しいために、色材 704 と微粒子 709 との接触確率が高められ、反応が比較的均一に、且つ充分に進行し、より均一で画像の濃度と彩度とに優れた画像が形成される。

【0042】 また、液体組成物 706 が被記録媒体 703 に付与された際（図 7（1））や、液溜り 707 にインク 713 が付与された際には（図 7（2））、微粒子

709 を分散させている分散媒が変化することによって微粒子 709 の分散が不安定となり、色材 704 が吸着する前に微粒子 709 間で凝集を起こすものも存在する。ここでいう分散媒の変化とは、2 種若しくはそれ以上の異種の液体が混合したときに一般的に観察される変化、例えば液相の pH や固形分濃度、溶剤組成、溶存イオン濃度等の物性変化を指し、液体組成物が被記録媒体やインクと接触した際にこれらの変化が急激且つ複合的に生じて、微粒子の分散安定性を破壊し、凝集物を生成するものと考えられる。

【0043】 これらの凝集物は、後述する凝集物内部に形成される細孔に色材を取り込むことにより更なる発色性の向上に寄与すると推測される。また、これら液溜り 707 内で形成された凝集物は、被記録媒体に吸着しているものもあれば、液相内を動ける（流動性を有する）ものも存在するが、流動性を有するものは、前述の色材と微粒子との反応過程と同様に、微粒子凝集物表面に色材が単分子状態で吸着し、より大きな凝集塊を形成し、これも発色性の向上に寄与しているものである。

【0044】 また、本発明の液体組成物を用いることにより、前述の被記録媒体の表面近傍に存在する微粒子凝集物 711 が形成される際に、凝集物の内部にある程度の大きさの細孔が形成される。液溜り 707 の中で微粒子 709 に吸着しきれなかった色材 704 は、溶媒成分とともに細孔を通して微粒子凝集物 711 の内部へと浸透するものもある。その際、色材 605 は微粒子凝集物内の細孔の入口付近や細孔内壁に吸着していくことによって、より多くの色材が微粒子凝集物 711 の表面や内部に効率よく吸着される。更に色材 704 が染料の場合、微粒子凝集物 711 の細孔直径は色材 704 のインク中で存在している分子サイズの 1 ～ 数倍程度であるために、細孔内部に吸着した色材 704 は、色材同士の凝集が極めて起こり難く、理想的な単分子状態を形成することが可能となる。このことが発色性の更なる向上に大きく寄与し、より一層広い色再現範囲を有する記録物を得ることができる。

【0045】 また、微粒子凝集物 711 の細孔物性は、液体組成物中に含まれる微粒子だけでなく、溶媒組成等によっても影響されることが分かり、液体組成物から微粒子凝集物を形成し、この微粒子凝集物のある特定の細孔半径領域における細孔容積が、被記録媒体上で形成される画像形成能と非常に相関性が高いことを見出した。

【0046】 更にモノマー 705 は、外部からのエネルギー 716 により、モノマー 705 は着色部 700 内全体で重合するとともに三次元架橋したポリマーに転化して固化し、被記録媒体に密着する（図 7（4））。その際、あらかじめ溶媒成分を除去するために乾燥過程を施すことにより、効果的に着色部 700 を硬化した強固なものとすることができる。この硬化過程によって着色部 700 は、被記録媒体 703 に強固に接着し、耐擦過性

や耐候性の向上が可能となる。

【0047】尚、これまで、液体組成物及びインクの順で、これらを被記録媒体に付与した場合で説明してきたが、インクと液体組成物との液-液反応が達成されれば、インクと液体組成物との被記録媒体への付与順はこれに何ら限られるものでなく、先ずインクを。次いで液体組成物を付与する順であってもよい。

【0048】以下に本発明を特徴づける液体組成物及びインクについて詳細に説明する。先ず、本発明におけるカチオン性のインク若しくはアニオン性のインクの定義について述べる。インクのイオン特性についていうとき、インク自体は荷電されておらず、それ自体では中性であることは、当該技術分野においてよく知られていることである。ここでいうアニオン性のインク若しくはカチオン性のインクとは、インク中の成分、例えば、色材がアニオン性基若しくはカチオン性基を有し、インク中において、これらの基がアニオン性基又はカチオン性基として挙動するように調整されているインクを指すものである。また、アニオン性又はカチオン性の液体組成物に関してもその意味は上記と同様である。

【0049】＜液体組成物＞以下に本発明の液体組成物について説明する。

（微粒子の作用）本発明において、液体組成物中に含まれる微粒子に望まれる作用としては、

1) インクと混合した際に、色材の本来持つ発色性を損なわずに、色材を吸着すること、
2) インクと混合した際、或いは被記録媒体に付与された際に、分散安定性が低下して、被記録媒体の表面に残存すること、
等が挙げられる。これらの作用は1種若しくは2種以上の微粒子によって達成されてもよい。

【0050】1) の作用を満たすための性質として、例えば、微粒子が色材と逆のイオン性を呈することが挙げられる。これにより、微粒子は色材を静電的に吸着できる。色材がアニオン性の場合、カチオン性の微粒子を用い、逆に色材がカチオン性の場合にはアニオン性の微粒子が用いられる。イオン性以外に色材を吸着する要素としては、微粒子のサイズや質量或いは表面の形状が挙げられる。例えば、表面に多数の細孔を持つ多孔質微粒子は、特有の吸着特性を示し、細孔の大きさや形状等、複数の要素によって色材を吸着できる。

【0051】2) の作用は、インクや被記録媒体との相互作用によって引き起こされる。このため、各構成により達成されればよいが、例えば、微粒子の性質として、インク組成成分や被記録媒体の構成成分と逆のイオン性を呈することが挙げられる。また、インク中或いは液体組成物中に電解質を共存させることによっても、微粒子の分散安定性は影響を受ける。本発明において、上記

1) と2) の作用のどちらか一方の作用が、瞬時に得られることが望ましい。更には、上記1) と2) と両方の

作用が瞬時に得られることが好ましい。

【0052】（微粒子凝集物）先に記録のメカニズムで述べたが、本発明の液体組成物を画像形成に用いた場合においては、含有されている特定の微粒子によって被記録媒体の表面近傍に微粒子凝集物が形成されるが、かかる凝集物の内部には、ある程度の大きさの細孔が形成される。すると、インク中で単独に存在していた色材は、被記録媒体内部へとインクが浸透していく際に、この微粒子凝集物の細孔内部へと浸透し、細孔の入口付近や内壁に、理想的な単分子状態で吸着されるので、色材は、より多く被記録媒体の表面近傍に残留することになり、これによって、より一層優れた発色性を有する記録物を得ることが可能となる。

【0053】従って、本発明の液体組成物は、画像形成の際に、微粒子凝集物内に適度な細孔が形成されるように構成することが好ましい。ここで、液体組成物中に含有される微粒子によって形成される細孔は、下記の方法で測定することができる。即ち、少なくとも微粒子と溶媒を含む液体組成物から得られる微粒子凝集物につい

て、下記の方法で、ある特定の細孔半径領域における細孔容積を測定し、かかる値が好適な範囲内となるように構成することによって、上記した記録のメカニズムが実行され、良好な画像形成が可能となる。これらの微粒子凝集物の物性を測定するにあたっては、先ず、測定対象である液体組成物を以下の手順で前処理する。

【0054】（1）微粒子が含有されている液体組成物を大気雰囲気下120℃で10時間乾燥して、ほぼ溶媒分を蒸発させて乾燥する。

（2）上記乾燥物を120℃から700℃まで1時間で昇温させた後、700℃で3時間焼成する。

（3）焼成後、上記焼成物を徐々に常温に戻し、焼成物を粉体化する。

ここで上記前処理を施す理由は、乾燥によって液体組成物から微粒子凝集物を形成させ、焼成によって液体組成物中の溶媒成分を完全に除去して、凝集物の内部の細孔を空にして空隙を形成するためである。

【0055】本発明では、微粒子凝集物の細孔の細孔半径と細孔容積の測定方法としては、窒素吸着脱離法を好適に用いることができる。本発明では、このような方法で測定した微粒子凝集物の細孔のサイズが、細孔半径が3nm～30nmの領域における細孔容積が特定の範囲にある場合に、良好な画像形成が可能となることがわかった。この細孔のサイズ領域における細孔容積が、画像形成能に対して相関性が高い理由は明確ではないが、推測するに、細孔半径を上記したような範囲とした場合には、微粒子凝集物の内部への色材や溶媒成分の浸透が生じ易いため、細孔に起因した色材の吸着が多くなること、及び、細孔自体の光散乱が抑えられることによって、実質的な発色性の向上に関与する色材量が増えるためであると考えられる。

【0056】従って、上記のような前処理を測定対象の液体組成物に行った場合に形成される微粒子凝集物について、細孔半径が3 nm～30 nmの領域と、30 nmを超える領域での細孔容積を測定することが、液体組成物を用いて形成した形成画像の発色性能の測定方法として効果的である。この領域における細孔物性の測定方法としては、窒素吸着脱離法による方法が最も好ましい。細孔半径と細孔容積は、上記した前処理した液体組成物試料を120℃で8時間真空脱気した後、窒素吸着脱離法よりBarrettらの方法(J. Am. Chem. Soc., Vol 73, 373, 1951)から求めることができる。更に好ましい測定方法は、微粒子凝集物に形成された細孔について、細孔半径が3 nm～20 nmの領域と、20 nmを超える領域での細孔容積を測定することである。この範囲では、色材が染料である場合に、特に、より一層の発色性の向上が得られるため、かかる発色性能を測定するうえで好ましい。

【0057】(微粒子凝集物の細孔半径及び細孔容積) 微粒子凝集物の細孔半径は前述の如く、色材の速やかな浸透と細孔入口付近や内壁への吸着及び細孔内部での色材の凝集を防ぐ観点から、3 nm～30 nmの範囲であることが好ましいと考えられる。また、発色性の向上に寄与するだけの色材を内部に取り込むためには、同時に、ある程度の容量が必要である。また、細孔容積が増すことで微粒子凝集物内の細孔の数も増加すると考えられ、細孔内部への色材の吸着量だけでなく、細孔の入口付近での吸着量も増加すると考えられる。

【0058】よって、これらの観点から、本発明に好適に用いられる液体組成物は、前記したような方法で微粒子凝集物内の細孔を測定した場合に、細孔半径が3 nm～30 nmの範囲における細孔容積が0.4 ml/g以上で、細孔半径が30 nmを超える領域での細孔容積が0.1 ml/g以下であるものが好ましい。細孔半径が3 nmよりも小さい細孔では、色材や溶媒成分が細孔内部に浸透しにくく、実質的に微粒子凝集物の細孔が発色性の向上に寄与しない。また、細孔半径が30 nmを超える領域において細孔容積が0.1 ml/gを超える場合には、光散乱が大きな細孔が多いために、細孔入口付近や内壁に吸着した色材が発色性に寄与しにくくなる。また、上記細孔半径の領域内での細孔容積が、この範囲未満である場合には、微粒子凝集物の内部へ浸透する色材や溶媒成分が少ないために、細孔の入口付近や内部に吸着する色材量が少なくなり、発色性の向上に対する寄与が低くなるので好ましくない。

【0059】より好ましい範囲としては、細孔半径が3 nm～20 nmの範囲における細孔容積が0.4 ml/g以上で、細孔半径が20 nmを超える領域での細孔容積が0.1 ml/g以下であるものを使用することが好ましい。細孔が3 nm～20 nmの半径の範囲の細孔が多く存在することによって、特に、色材に染料を用いた

場合において、発色性は更に向上し、より一層広い色再現範囲を有する画像が形成できる。液体組成物から形成される微粒子凝集物の細孔半径や細孔容積は、含まれる微粒子の化学種や形状、大きさばかりでなく、溶剤種やその他の添加物及びそれらの組成比等により変化し、これらの条件を制御することによって微粒子凝集物の形成状態をコントロールできると考えられる。従って、本発明の液体組成物を作製する場合には、これらのことを勘案して、微粒子凝集物内に形成される細孔の形状が上記の範囲内となるようにすることが好ましい。

【0060】次に、カチオン性又はアニオン性微粒子を含有する液体組成物について具体的に説明する。

〔カチオン性液体組成物〕カチオン性の液体組成物としては、例えば、カチオン性基を表面に有する微粒子を含み、該微粒子が安定に分散されてなる液体組成物が挙げられる。本発明においては、カチオン性の液体組成物として、例えば、酸を含みpHが2～7に調整されたもの、また、ゼータ電位が+5～+90 mVのものを好適に用いることができる。

【0061】(pH及びゼータ電位について) 液体組成物のゼータ電位について述べる。ゼータ電位の基本原理について以下に示す。一般に、固体が液体中に分散している系において、固相の表面に遊離電荷がある場合、固相界面付近の液相には反対電荷の荷電層が電気的中性を保つように現れる。これは電気的二重層と呼ばれ、この電気的二重層による電位差のことをゼータ電位と呼んでいる。ゼータ電位がプラスである場合、微粒子の表面はカチオン性を示し、マイナスではアニオン性を示す。一般に、その絶対値が高いほど微粒子間に働く静電的反発力が強くなり、分散性がよいと言われ、同時に微粒子表面のイオン性が強いことが考えられる。即ち、カチオン性微粒子のゼータ電位が高いほどカチオン性が強く、インク中のアニオン性化合物を引き付ける力が強いと言える。

【0062】本発明者らが鋭意検討した結果、ゼータ電位が+5～+90 mVの範囲にある液体組成物を用いた場合に、被記録媒体上に形成してなる着色部が、特に優れた発色特性を呈することを見出した。その理由は定かではないが、おそらく、微粒子のカチオン性が適度であるために、急速なアニオン性化合物(アニオン性色材)の凝集が起こらずに、アニオン性化合物が微粒子表面に薄く均一に吸着するので、色材が巨大なレーキを形成しにくく、その結果、色材本来の発色特性がより良好な状態で発現されるものと考えられる。更に本発明のカチオン性の液体組成物では、アニオン性化合物を微粒子表面に吸着した後も、微粒子が弱いカチオン性を呈しつつ分散不安定状態となることで、微粒子が凝集しながら被記録媒体の表面に容易に吸着されて、被記録媒体の表面近傍に残り易くなっていると考えられる。

【0063】この結果、以下に挙げる優れた効果が得ら

れるものと考えられる。即ち、普通紙のみならず、吸液性の乏しいプラスチックや金属等の媒体に対してもインクジェット用コート紙並みの優れた発色特性と、シャドウ部やベタ部等のインク付与量が多い画像領域において、白モヤや色ムラが少なく、色の均一性に優れたものとなる。また、コート紙と比べて極めて効率よく微粒子にアニオン性化合物が吸着し発色するために、カチオン性微粒子の付与量も少なくできるので、とりわけ普通紙に印字した場合には、紙の風合いを損なうことがなく、記録画像の耐擦過性にも優れる。より好ましいゼータ電位の範囲としては、例えば、ゼータ電位が+10〜+85 mVの範囲にあるカチオン性微粒子を含む液体組成物を使用した場合には、ベタ印字した際にドット間の境界が目立ち難くなり、ヘッドスキャンによるスジムラのより一層の低減を達成することができ、更には、ゼータ電位が+15〜+65 mVの範囲にある、カチオン性微粒子を含む液体組成物を使用すると、媒体種によらず、極めて優れた発色性を有する画像を得ることが可能となる。

【0064】本発明のカチオン性の液体組成物のpHは、保存安定性とアニオン性化合物の吸着性の観点から、25℃付近で2〜7の範囲にあることが好ましい。このpHの範囲内においては、液体組成物をアニオン性のインクと混合した際に、アニオン性化合物の安定性を著しく低下させることがないため、アニオン性化合物同士の高い凝集を引き起こすことがなく、記録画像の彩度が下がったり、くすんだ画像となることを有効に防止することができる。また、上記範囲内であるとカチオン性微粒子の分散状態も良好であるので、液体組成物の保存安定性や記録ヘッドからの吐出安定性を良好に維持することができる。更にはインクと混合した際に、アニオン性物質がカチオン性微粒子表面に十分に吸着されるので、優れた発色性のインクジェット記録物を得られる。より好ましいpHの範囲としては、pHが3〜6であり、この範囲では、長期保存による記録ヘッドの腐食を極めて有効に防止できるとともに、記録画像の耐擦過性もより一層向上する。

【0065】(カチオン性微粒子)次に、本発明のカチオン性の液体組成物を構成する成分について述べる。第1の成分として挙げられるカチオン性の微粒子は、上記した作用効果を達成するために、液体組成物中に分散された状態において粒子自体の表面がカチオン性を呈することを要する。表面をカチオン性とすることによって、アニオン性のインクと混合した際に、アニオン性の色材が粒子表面に速やかに吸着し、色材を単分子状態で均一に被記録媒体表面に残すことにより十分な画像濃度のインクジェット記録物を得られる。これに対し、微粒子表面がカチオン性でなく、且つ液体組成物の中で、微粒子と水溶性のカチオン性化合物とが別々に存在しているような場合には、カチオン性化合物を中心に色材が凝集を

起こし、色材自体の発色特性を損なうためにインクジェット用コート紙並みの発色性を達成することが困難となる。そのため本発明の液体組成物に用いられる微粒子は、その表面がカチオン性である必要があるが、本質的にカチオン性である微粒子は勿論のこと、本来は静電的にアニオン性或いは中性である微粒子であっても、処理によって表面がカチオン化された微粒子であれば、本発明の液体組成物に用いることができる。

【0066】本発明で好適に用いられるカチオン性微粒子は、被記録媒体上で形成されるこれらの微粒子による凝集物に細孔が形成されるものであれば、本発明の目的を達成するに十分であるために、特に微粒子の材料種には限定されない。具体例としては、例えば、カチオン化した、シリカ、アルミナ、アルミナ水和物、チタニア、ジルコニア、ボリア、シリカボリア、セリア、マグネシア、シリカマグネシア、炭酸カルシウム、炭酸マグネシウム、酸化亜鉛、ハイドロタルサイト等やこれらの複合微粒子や有機微粒子、無機有機複合微粒子等が挙げられる。これらのカチオン性微粒子は、1種又は2種以上を混合して使用することができる。

【0067】特に微粒子としてアルミナ水和物を用いた場合は粒子表面が正電荷をもっているために好ましく、中でもX線回折法で、ペーマイト構造を示すアルミナ水和物が優れた発色性や色の均一性、保存安定性等の点で好ましい。アルミナ水和物は下記的一般式により定義される。



上記式中、nは0〜3の整数の1つを表し、mは0〜10、好ましくは0〜5の値を有する。mH₂Oの表現は、多くの場合に結晶格子の形成に関与しない脱離可能な水相を表すものであり、そのために、mは整数でない値をとることもできる。但し、mとnは同時に0とはならない。

【0068】一般にペーマイト構造を示すアルミナ水和物の結晶は、その(020)面が巨大平面を形成する層状化合物であり、X線回折図形に特有の回折ピークを示す。完全ペーマイトの他に擬ペーマイトと称する、過剰な水を(020)面の層間に含んだ構造をとることもできる。この擬ペーマイトのX線回折図形はペーマイトよりもブロードな回折ピークを示す。

【0069】ペーマイトと擬ペーマイトは明確に区別のできるものではないので、本発明では特に断わらない限り、両者を含めてペーマイト構造を示すアルミナ水和物(以下アルミナ水和物という)という。(020)面が面間隔及び(020)の結晶厚さは、回折速度2θが14〜15°に現れるピークを測定して、ピークの回折角度2θと半値幅Bから、面間隔はブラッグ(Bragg)の式で、結晶厚さはシェラー(Scherrer)の式を用いて求めることができる。(020)面の面間隔はアルミナ水和物の親水性・疎水性の目安として用いることができ

る。本発明で用いるアルミナ水和物の製造方法としては、特に限定されないが、ペーマイト構造をもつアルミナ水和物を製造できる方法であれば、例えば、アルミニウムアルコキシドの加水分解、アルミン酸ナトリウムの加水分解等の公知の方法で製造することができる。

【0070】特開昭56-120508号公報に開示されているように、X線回折的に無定形のアルミナ水和物を、水の存在下で50℃以上で加熱処理することによってペーマイト構造に変えて用いることができる。特に好ましく用いることができる方法は、長鎖のアルミニウムアルコキシドに対して酸を添加して加水分解・解膠を行うことによってアルミナ水和物を得る方法である。ここで、長鎖のアルミニウムアルコキシドとは、例えば、炭素数が5以上のアルコキシドであり、更に炭素数12～22のアルコキシドを用いると、後述するように製造過程におけるアルコール分の除去及びアルミナ水和物の形状制御が容易になるために好ましい。

【0071】添加する酸としては有機酸及び無機酸の中から1種又は2種以上を自由に選択して用いることができるが、加水分解の反応効率及び得られたアルミナ水和物の形状制御や分散性の点で硝酸が最も好ましい。この過程の後に水熱合成等を行って粒子径を制御することも可能である。硝酸を含むアルミナ水和物の分散液を用いて水熱合成を行うと、水溶液中の硝酸がアルミナ水和物表面に硝酸根として取り込まれ、該水和物の水分散性を向上させることができる。また、水熱合成の後、アルミナ水和物スラリーに適宜酸を加えてpHを調整し、濃縮することで、少量の酸濃度で極めて安定な高固形分濃度のアルミナ水和物スラリーを調製することができる。こうしたスラリーを用いた場合は、後述する酸を別途添加する必要なくアルミナ水和物微粒子の分散安定性に優れた液体組成物を作製することができる。

【0072】上記アルミニウムアルコキシドの加水分解による方法は、アルミナヒドロゲルやカチオン性アルミナを製造する方法と比較して、各種イオン等の不純物が混入し難いという利点がある。更に長鎖のアルミニウムアルコキシドは加水分解後の長鎖のアルコールが、例えば、アルミニウムイソプロキシド等の短鎖のアルコキシドを用いる場合と比較して、アルミナ水和物の脱アルコールを完全に行うことができるという利点もある。加水分解の開始時の溶液のpHは6未満に設定することが好ましい。pHが8を越えると最終的に得られるアルミナ水和物が結晶質になるので好ましくない。

【0073】また、本発明で用いられるアルミナ水和物としては、X線回折法でペーマイト構造を示すものであれば、二酸化チタン等の金属酸化物を含有したアルミナ水和物を用いることもできる。二酸化チタン等の金属酸化物の含有比率は、アルミナ水和物の0.01～1.00質量%が光学濃度が高くなるので好ましく、より好ましくは0.13～1.00質量%であり、色材の吸着速

度が速くなって、しみやビーディングが発生し難くなる。更に前記二酸化チタンはチタンの価数が+4価であることが必要である。二酸化チタンの含有量は、硼酸に融解してICP法で調べることができる。また、アルミナ水和物中の二酸化チタンの分布とチタンの価数は、ESCAを用いて分析することができる。

【0074】アルミナ水和物の表面をアルゴンイオンで100秒及び500秒エッチングして、チタンの含有量の変化を調べるることができる。二酸化チタンはチタンの価数が+4価よりも小さくなると、二酸化チタンが触媒として働くようになって記録画像の耐候性が低下したり、記録画像の黄変が起りやすくなることがある。

【0075】二酸化チタンの含有は、アルミナ水和物の表面近傍だけでもよいが、内部まで含有していてもよい。また、含有量が表面から内部にかけて変化していてもよい。表面のごく近傍にのみ二酸化チタンが含有されていると、アルミナ水和物の電気的特性が維持され易いので、更に好ましい。

【0076】二酸化チタンを含有したアルミナ水和物の製造方法としては、例えば、学会出版センター刊「表面の科学」第327頁（田丸謙二編、1985年）に記載されているような、アルミニウムアルコキシドとチタンアルコキシドの混合液を加水分解して製造する方法が好ましい。その他の方法としては前記アルミニウムアルコキシドとチタンアルコキシドの混合液を加水分解するときに、結晶成長の核としてアルミナ水和物を添加して製造することもできる。

【0077】二酸化チタンの代わりにシリカ、マグネシウム、カルシウム、ストロンチウム、バリウム、亜鉛、硼素、ゲルマニウム、錫、鉛、ジルコニウム、インジウム、燐、バナジウム、ニオブ、タンタル、クロム、モリブデン、タングステン、マンガン、鉄、コバルト、ニッケル、ルテニウム等の酸化物を含有させて用いることができる。例えば、シリカを含有したアルミナ水和物は記録画像の耐擦過性の向上に効果がある。

【0078】本発明に好適に用いられるアルミナ水和物は、その(020)面の面間隔が0.614～0.626nmの範囲のものであり、この範囲内では液体組成物中でのアルミナ水和物粒子の分散安定性が良好で、保存安定性や吐出安定性に優れた液体組成物が得られる。この理由は定かでないが、(020)面の面間隔が上記範囲内であれば、アルミナ水和物の疎水性及び親水性の両比率が適度な範囲であるため、液体組成物中で粒子同士の適度な反発による分散安定や吐出口内部での濡れ性のバランスが適度であることにより、液体組成物の吐出安定性が良好になるものと推測している。

【0079】また、アルミナ水和物は、その(020)面の結晶厚さが4.0～10.0nmの範囲が好ましく、この範囲内であると透明性や色材の吸着性が優れるために好ましい。本発明者らの知見によれば、(02

0) 面の面間隔と (020) 面の結晶厚さは相関があるので、(020) 面の面間隔が上記範囲内であれば (020) 面の結晶厚さを 4.0~10.0 nm の範囲に調整することができる。

【0080】更に、上記アルミナ水和物、金属アルミニウム或いはアルミニウム塩等を焼成 (calcination) 等の熱処理により生成されるアルミナ (酸化アルミニウム) も同様に正電荷をもつため好適に用いられる。アルミナとしては α 型、 γ 型、更に δ 、 χ 、 η 、 ρ 、 β 型等の結晶状態を持つものがあり、表面がカチオン性に保たれた形で、水中にて安定的に分散するものであればいずれも用いることができる。中でも γ 型は表面が活性で、色材の吸着力が高く、比較的微粒化された安定な微粒分散体も形成しやすいため、発色性、保存性、吐出安定性等に優れ、好適に用いることができる。

【0081】また、本発明で使用する上記したようなカチオン性微粒子は、印字後の発色性、色の均一性及び保存安定性等の観点から、動的光散乱方式により測定される平均粒子直径が 0.005~1 μ m の範囲のものが好適に用いられる。この範囲内では、普通紙のような吸液性の高い被記録媒体の内部へ過度の浸透を有効に防ぐことができ、発色性や色の均一性の低下を抑えることができる。また、カチオン性微粒子が液体組成物中で沈降することも抑えられ、液体組成物の保存安定性の低下も有効に防止することができる。より好ましくは平均粒子直径が 0.01~0.8 μ m の範囲内のものであり、このような微粒子を用いれば、被記録媒体に印字した後の画像の耐擦過性や記録物の質感が特に好ましいものとなる。更に好ましくは平均粒子直径が 0.03~0.3 μ m の範囲内のものであり、このような微粒子は被記録媒体上で形成される微粒凝集物の細孔が、目的とする細孔半径領域において効果的に形成されやすいために好ましい。

【0082】(カチオン性微粒子の細孔物性・形状) また、本発明で使用する上記したようなカチオン性微粒子は、被記録媒体上で形成される微粒凝集物の細孔を効率的に形成すると同時に、微粒自体の表面に色材を効率よく吸着させるうえにおいて、窒素吸着脱離法における微粒子の極大細孔半径が 2~12 nm で、全細孔容積が 0.3 ml/g 以上であるものが好ましい。より好ましくは微粒子の極大細孔半径が 3~10 nm で、全細孔容積が 0.3 ml/g 以上であるものが、被記録媒体上で形成される微粒凝集物の細孔が、目的とする細孔半径領域において効果的に形成されやすいために好ましい。

【0083】本発明で使用する上記微粒子は、その BET 比表面積が 70~300 m²/g の範囲内であると、微粒表面への色材の吸着点が十分存在することによって、単分子状態で色材をより効果的に被記録媒体の表面近傍に残しやすくなり、発色性の向上に寄与する。

【0084】また、本発明で使用する微粒子の形状は、微粒子をイオン交換水に分散させてコロジオン膜上に滴下して測定用試料を作製し、透過型電子顕微鏡で観察して求めることができる。本発明においては被記録媒体上で微粒凝集物を形成させる際に凝集物内に細孔を形成させる点で、微粒形状が針状や平板形状、若しくは球状の一次粒子が、ある方向性を持って繋がった二次粒子を形成している棒状やネckレス状等の非球形状のものを好適に用いることができる。

【0085】本発明者らの知見によれば、微粒子の形状は、平板状の方が針状や毛状束 (纖毛状) よりも水への分散性が良く、微粒凝集物を形成した場合に微粒子の配向がランダムになるために細孔容積が大きくなるのでより好ましい。ここで毛状束形状とは針状の微粒子が側面同士を接して髪の毛の束のように集まった状態をいう。特に本発明で好ましく用いることができるアルミナ水和物の中でも擬ペーマイトには文献 (Rocek J., et al, Applied Catalysis, 74 巻、29~36 頁、1991 年) に記載されているように、纖毛状とそれ以外の形状があることが一般に知られている。

【0086】平板形状の粒子のアスペクト比は、特公平 5-16015 号公報に定義されている方法で求めることができる。アスペクト比は、粒子の厚さに対する直径の比で示される。ここで直径とは、アルミナ水和物を顕微鏡又は電子顕微鏡で観察したときの粒子の投影面積と等しい面積を有する円の直径を示すものとする。縦横比は、アスペクト比と同じように観察して平板面の最小値を示す直径と最大値を示す直径の比で表わされる。また、毛状束形状の場合には、アスペクト比を求める方法は、毛状束を形成する個々の針状のアルミナ水和物粒子を円柱として、上下の円の直径と長さをそれぞれ求めて、その比をとって求めることができる。最も好ましいアルミナ水和物の形状は、平板状では平均アスペクト比が 3~10 の範囲が、また、毛状束では平均アスペクト比が 3~10 の範囲が好ましい。平均アスペクト比が上記範囲内であれば、微粒凝集物を形成したときに粒子間に隙間が形成され易いため多孔質構造を容易に形成することができる。

【0087】本発明の液体組成物中における上記したようなカチオン性微粒子の含有量は、使用する物質の種類により、最適な範囲を適宜決定すればよいが、0.1~40 質量% の範囲が本発明の目的を達成するうえで好適な範囲であり、より好ましくは 1~30 質量%、更には 3~15 質量% の範囲が好適である。このような範囲内では、媒体種によらず優れた発色の画像を安定に得ることができ、また、液体組成物の保存安定性や吐出安定性にも特に優れている。

【0088】(酸) 先に述べたように、本発明の液体組成物は、酸を含み、pH が 2~7 に調整されたものであることが好ましい。酸は、カチオン性微粒表面をイオ

ン化し、表面電位を高めることにより、液中での微粒子の分散安定性を向上させるとともに、インク中のアニオン性化合物（アニオン性色材）の吸着性向上や、液体組成物の粘度調整の役割を果たす。本発明に好適に用いられる酸は、使用するカチオン性微粒子と組み合わせて、所望の pH やゼータ電位或いは微粒子分散性等の物性が得られるものであれば特に限定されず、下記に挙げる無機酸や有機酸等から自由に選択して使用することができる。

【0089】具体的には、無機酸としては、例えば、塩酸、硫酸、亜硫酸、硝酸、亜硝酸、リン酸、硼酸、炭酸等が挙げられ、有機酸としては、例えば、下記に挙げるようなカルボン酸やスルホン酸、アミノ酸等が挙げられる。

【0090】カルボン酸としては、例えば、ギ酸、酢酸、クロロ酢酸、ジクロロ酢酸、トリクロロ酢酸、フルオロ酢酸、トリメチル酢酸、メトキシ酢酸、メルカプト酢酸、グリコール酸、プロピオン酸、酪酸、吉草酸、カプロン酸、カプリル酸、カプリン酸、ラウリン酸、ミリスチン酸、パルミチン酸、ステアリン酸、オレイン酸、リノール酸、リノレン酸、シクロヘキサンカルボン酸、フェニル酢酸、安息香酸、*o*-トルイル酸、*m*-トルイル酸、*p*-トルイル酸、*o*-クロロ安息香酸、*m*-クロロ安息香酸、*p*-クロロ安息香酸、*o*-ブプロモ安息香酸、*m*-ブプロモ安息香酸、*p*-ブプロモ安息香酸、*o*-ニトロ安息香酸、*m*-ニトロ安息香酸、*p*-ニトロ安息香酸、シュウ酸、マロン酸、コハク酸、グルタル酸、アジピン酸、酒石酸、マレイン酸、フマル酸、クエン酸、フタル酸、イソフタル酸、テレフタル酸、サリチル酸、*p*-ヒドロキシ安息香酸、アントラニル酸、*m*-アミノ安息香酸、*p*-アミノ安息香酸、*o*-メトキシ安息香酸、*m*-メトキシ安息香酸、*p*-メトキシ安息香酸等が挙げられる。

【0091】また、スルホン酸としては、例えば、ベンゼンスルホン酸、メチルベンゼンスルホン酸、エチルベンゼンスルホン酸、ドデシルベンゼンスルホン酸、2, 4, 6-トリメチルベンゼンスルホン酸、2, 4-ジメチルベンゼンスルホン酸、5-スルホサリチル酸、1-スルホナフタレン、2-スルホナフタレン、ヘキサンスルホン酸、オクタンスルホン酸、ドデカンスルホン酸等が挙げられる。

【0092】また、アミノ酸としては、グリシン、アラニン、バリン、 α -アミノ酪酸、 γ -アミノ酪酸、 β -アラニン、タウリン、セリン、 ϵ -アミノ-*n*-カプロン酸、ロイシン、ノルロイシン、フェニルアラニン等が挙げられる。

【0093】そして、本発明の液体組成物においては、これらの酸を1種又は2種以上混合して使用することができる。これらの酸の中でも、水中での一次解離定数 pK_a が5以下のものは、カチオン性微粒子の分散安定性

やアニオン性化合物の吸着性に特に優れるため、好適に用いることができる。このような酸としては、具体的には、塩酸、硝酸、硫酸、リン酸、酢酸、ギ酸、シュウ酸、乳酸、クエン酸、マレイン酸、マロン酸等が挙げられる。

【0094】本発明の液体組成物では、液体組成物中におけるカチオン性微粒子（A）と酸（B）の混合比率を、質量基準で $A : B = 200 : 1 \sim 5 : 1$ 、より好ましくは $150 : 1 \sim 8 : 1$ の範囲となるようにすることが、カチオン性微粒子の分散安定性の向上及びアニオン性化合物の微粒子表面への吸着性の向上を図るうえで好ましい。

【0095】（他の構成成分）次に、カチオン性の液体組成物を構成するその他の成分について具体的に説明する。本発明のカチオン性の液体組成物は、上記したカチオン性微粒子と、好ましくは上記したような酸や光重合開始剤等を含み、その他に、通常は液媒体として水を含むが、更に後述のモノマーを溶解するための有機溶剤及びその他の添加剤を含むものが好ましい。

【0096】この際に使用する有機溶剤としては、例えば、ジメチルホルムアミド、ジメチルアセトアミド等のアミド類：アセトン等のケトン類：テトラヒドロフラン、ジオキサン等のエーテル類、ポリエチレングリコール、ポリプロピレングリコール等のポリアルキレングリコール類：エチレングリコール、プロピレングリコール、ブチレングリコール、トリエチレングリコール、1, 2, 6-ヘキサントリオール、チオジグリコール、ヘキシレングリコール、ジエチレングリコール等のアルキレングリコール類：エチレングリコールメチルエーテル、ジエチレングリコールモノメチルエーテル、トリエチレングリコールモノメチルエーテル等の多価アルコールの低級アルキルエーテル類：エタノール、イソプロピルアルコール、*n*-ブチルアルコール、イソブチルアルコール等の1価アルコール類の他に、グリセリン、*N*-メチル-2-ピロリドン、1, 3-ジメチル-イミダゾリジノン、トリエタノールアミン、スルホラン、ジメチルスルホキシド等：ベンゼン、トルエン、キシレン等の芳香族炭化水素類：ヘキサン、オクタン、ヘプタン等の脂肪族炭化水素類：プロピレンカーボネート等が挙げられる。上記有機溶剤の含有量については特に制限はないが、例えば、液体組成物全質量の5~90%、更には5~60%が好適な範囲である。

【0097】また、本発明の液体組成物には、更に、必要に応じて、粘度調整剤、pH調整剤、防腐剤、各種界面活性剤、酸化防止剤及び蒸発促進剤、水溶性カチオン性化合物やバインダー樹脂等の添加剤を適宜に配合しても構わない。界面活性剤の選択は、液体組成物の被記録媒体への濡れや浸透性を調整するうえで特に重要である。水溶性カチオン性化合物は、液体組成物のカチオン性の更なる付与等、例えば、異色画像領域でのブリード

の抑制や文字品位の向上等を目的に、本発明の作用効果を阻害しない範囲において自由に選択し添加できる。

【0098】水溶性カチオン性化合物としては、具体的には、例えば、ポリアリルアミン、ポリアミンスルホン、ポリビニルアミン、キトサン、及びこれらの塩酸或いは酢酸等の酸による中和物又は部分中和物、高分子のノニオン性化合物の一部をカチオン化した化合物、例えば、ビニルピロリドンとアミノアルキルアルキレート4級塩との共重合体、アクリルアミドとアミノメチルアクリルアミド4級塩との共重合体等やその他カチオン性界面活性剤等の1級、2級及び3級アミン塩型の化合物やアミノ酸型両性化合物等から1種若しくは2種以上を選択して使用することができる。

【0099】バインダー樹脂は、カチオン性微粒子の更なる耐擦過性の向上等の目的で、被記録媒体の質感や液体組成物の保存安定性や吐出安定性を損ねない範囲において併用することができ、例えば、水溶性ポリマーやポリマーエマルジョン、ポリマーラテックス等から自由に選択し、使用することができる。また、後述するように、光重合開始剤や増感剤を液体組成物中に添加することは、モノマーの硬化（エネルギーの付与によってモノマーが重合し、生成重合体が架橋すること）を効率的に促進させると同時に、液体組成物及びインクの保存安定性において好ましい形態である。

【0100】（液体組成物の表面張力）本発明の液体組成物は、無色或いは白色であることがより好ましいが、被記録媒体の色に合わせて調色してもよい。更に以上のような液体組成物の各種物性の好適な範囲としては、表面張力を $10 \sim 60 \text{ mN/m}$ (dyn/cm)、より好ましくは $10 \sim 40 \text{ mN/m}$ (dyn/cm) とし、粘度を $1 \sim 30 \text{ mPa} \cdot \text{s}$ (cP) としたものである。

【0101】〔アニオン性液体組成物〕本発明のアニオン性の液体組成物は、アニオン性基を表面に有する微粒子を必須の構成成分とし、該微粒子が安定に分散していることを特徴とするが、更には塩基を含み、pHが7～12に調整されているものや、ゼータ電位が $-5 \sim -90 \text{ mV}$ であるものが好ましい。

【0102】（pH及びゼータ電位について）本発明者らが鋭意検討した結果、ゼータ電位が $-5 \sim -90 \text{ mV}$ の範囲にあるアニオン性液体組成物は、インク中のカチオン性化合物（カチオン性色材）がアニオン性微粒子の表面に特に効率よく吸着され、被記録媒体上において特に優れた発色特性を呈することを見出した。その理由は定かではないが、おそらく先に説明したカチオン性液体組成物の場合と同様に、微粒子のアニオン性が適度であるために、インク中のカチオン性化合物の急速な凝集が起こらずに、微粒子表面に薄く均一に吸着することで色材が巨大なレーキを形成せず、色材本来の発色特性がよりよく発現されるものと考えられる。更に本発明のアニオン性の液体組成物においては、カチオン性化合物を微

粒子表面に吸着した後に分散不安定となり、被記録媒体上で溶媒成分が蒸発、浸透する際の濃度変化で微粒子同士が凝集して表面近傍に残り易くなるものと考えられる。

【0103】この結果、以下に挙げる優れた効果が得られるものと考えられる。即ち、インクジェット用コート紙並みの優れた発色特性とシャドウ部やベタ部等のインク付与量が多い画像領域において、白モヤや色ムラが少なく色の均一性に優れる。また、コート紙と比べて極めて効率よく微粒子表面にカチオン性化合物が吸着し、発色するために、アニオン性微粒子の付与量も少なくでき、とりわけ普通紙に印字した場合には紙の風合いが保たれ、記録画像の耐擦過性も良くなる。より好ましいゼータ電位の範囲は、 $-10 \sim -85 \text{ mV}$ の範囲であり、このような範囲のゼータ電位を有するアニオン性微粒子を含む液体組成物を使用した場合には、ベタ印字した際にドット間の境界が目立ち難くなり、ヘッドスキャンによるスジムラのより一層の低減を達成することができる。更に好ましくは、ゼータ電位が $-15 \sim -65 \text{ mV}$ の範囲にあるアニオン性微粒子を含む液体組成物を使用すると、被記録媒体種によらず、極めて優れた発色性を有する画像を得ることが可能となる。

【0104】本発明のアニオン性の液体組成物のpHは、保存安定性とインク中のカチオン性化合物の吸着性の観点から 25°C 付近で $7 \sim 12$ の範囲であることが好ましい。このpH範囲内においては、カチオン性のインクと混合した際に、カチオン性化合物（色材）の安定性を著しく低下させることがないため、カチオン性化合物同士の強い凝集を引き起こすことがなく、記録画像の彩度が下がったり、くすんだ画像となることを有効に防止することができる。また、pHが上記のような範囲内であれば、アニオン性微粒子の分散性も良好であるため、液体組成物の保存安定性や記録ヘッドからの吐出安定性を良好に維持することができる。更にはインクと混合した際に、カチオン性物質がアニオン性微粒子表面に十分に吸着され、優れた発色性のインクジェット記録物が得られる。より好ましい液体組成物のpHの範囲は $8 \sim 11$ であり、pHがこの範囲内であれば、長期保存による記録ヘッドの腐食を極めて有効に防止できるとともに、記録画像の耐擦過性もより一層向上する。

【0105】（アニオン性微粒子）次に、本発明のアニオン性の液体組成物を構成する成分について述べる。第1の必須成分として挙げられるアニオン性の微粒子は、上記した作用効果を達成するために、液体組成物中に分散された状態において微粒子自体の表面がアニオン性を呈するものであることが好ましい。微粒子表面をアニオン性とすることによってカチオン性のインクと混合した際に、カチオン性の色材を粒子表面に吸着でき、色材を単分子状態で均一に被記録媒体表面に残すことにより十分な画像濃度のインクジェット記録物が得られる。

【0106】これに対し、微粒子表面がアニオン性でなく、且つ液体組成物の中で、微粒子と水溶性のアニオン性化合物とが別々に存在している場合には、アニオン性化合物を中心に色材が凝集を起し、色材自体の発色特性を損なうために、インクジェット用コート紙並みの発色性を達成することが困難となる。そのため本発明の液体組成物で用いる微粒子は、表面がアニオン性に帯電していることが必要であるが、本質的にアニオン性である微粒子は勿論のこと、本来は静電的にカチオン性或いは中性の微粒子であっても、処理によって表面がアニオン化された微粒子であれば用いることができる。

【0107】本発明で好適に用いられるアニオン性微粒子は、被記録媒体上で形成されるこれらの微粒子による凝集物に細孔が形成されるものであれば本発明の目的を達成するに十分であり、特に微粒子の材料種は限定されない。具体例としては、例えば、アニオン化した、シリカ、チタニア、ジルコニア、ボリア、シリカボリア、セリア、マグネシア、シリカマグネシア、炭酸カルシウム、炭酸マグネシウム、酸化亜鉛等やこれらの複合微粒子や有機微粒子、無機有機複合微粒子等が挙げられる。そして、本発明の液体組成物においては、これらを1種又は2種以上混合して使用することができる。

【0108】また、本発明で使用するアニオン性微粒子は、先に説明したカチオン性微粒子の場合と同様に、印字後のインクの発色性、色の均一性及び保存安定性の観点から、動的分散方式により測定される平均粒子直径が0.005～1 μ mの範囲のものが好適である。より好ましくは平均粒子直径が0.01～0.8 μ mの範囲内のものであり、このような微粒子を用いれば、被記録媒体に印字した後の耐擦過性や質感が特に好ましいものとなる。更に好ましくは平均粒子直径が0.03～0.3 μ mの範囲内のものであり、このような微粒子は被記録媒体上で形成される微粒子凝集物の細孔が、目的とする細孔半径領域において効果的に形成されやすいために好ましい。

【0109】(アニオン性微粒子の細孔物性・形状)また、本発明で使用する上記したようなアニオン性微粒子は、被記録媒体上で形成される微粒子凝集物の細孔を効率的に形成すると同時に、微粒子自体の表面に色材を効率よく吸着させるうえで、窒素吸着脱離法による微粒子の極大細孔半径が2～12nmで、全細孔容積が0.3ml/g以上であるものが好ましい。より好ましくは微粒子の極大細孔半径が3～10nmで、全細孔容積が0.3ml/g以上であるものが、被記録媒体上で形成される微粒子凝集物の細孔が、目的とする細孔半径領域において効果的に形成されやすいために好ましい。

【0110】本発明で使用する微粒子は、そのBET比表面積が70～300m²/gの範囲内であると、微粒子表面への色材の吸着点が十分存在することによって単分子状態で色材をより効果的に被記録媒体の表面近傍に

残しやすくなり、発色性の向上に寄与する。

【0111】また、本発明で使用する微粒子の形状は、微粒子をイオン交換水に分散させてコロジオン膜上に滴下して測定用試料を作製し、透過型電子顕微鏡で観察して求めることができる。本発明においては被記録媒体上で微粒子凝集物を形成させる際に凝集物内に細孔を形成させる点で、微粒子は、針状や平板形状、若しくは球状の一次粒子がある方向性を持って繋がった二次粒子を形成している棒状やネックレス状等の非球形状のものを好適に用いることができる。本発明者らの知見によれば、微粒子は、平板状の形状の方が針状よりも水への分散性が良く、微粒子凝集物を形成した場合に微粒子の配向がランダムになるために細孔容積が大きくなるのでより好ましい。

【0112】上記したようなアニオン性微粒子の液体組成物中の含有量は、使用する物質の種類により、最適な範囲を適宜に決定すればよいが、0.1～40質量%の範囲とすることが本発明の目的を達成する上で好適な範囲であり、より好ましくは1～30質量%、更には3～15質量%の範囲が好適である。このような範囲内では、媒体種によらず、優れた発色の画像を安定に得ることができ、また、液体組成物の保存安定性や吐出安定性にも特に優れている。

【0113】(塩基)先に述べたように、本発明のアニオン性の液体組成物は、塩基を含み、pHが7～12に調整されたものであることが好ましい。塩基は、アニオン性微粒子表面をイオン化し、表面電位を高めることにより液中でのアニオン性微粒子の分散安定性を向上させるとともに、インク中のカチオン性化合物(カチオン性色材)の吸着性向上や液体組成物の粘度調整の役割を果たす。本発明に好適に用いられる塩基は、使用するアニオン性微粒子と組み合わせた場合に、所望のpH、ゼータ電位及び微粒子分散性等の物性が得られるものであれば特に限定はなく、下記に挙げるような無機化合物や有機化合物等から自由に選択して、使用することができる。

【0114】具体的には、例えば、水酸化ナトリウム、水酸化リチウム、炭酸ナトリウム、炭酸アンモニウム、アンモニア、酢酸ナトリウム、酢酸アンモニウム、モルホリン、モノエタノールアミン、ジエタノールアミン、トリエタノールアミン、エチルモノエタノールアミン、n-ブチルモノエタノールアミン、ジメチルエタノールアミン、ジエチルエタノールアミン、エチルジエタノールアミン、n-ブチルジエタノールアミン、ジノルマルブチルエタノールアミン、モノイソプロパノールアミン、ジイソプロパノールアミン、トリイソプロパノールアミン等のアルカノールアミンを用いることができる。これらの中でも特に、塩基の水中での一次解離定数pK_bが5以下の塩基は、アニオン性微粒子の分散安定性やカチオン性化合物(カチオン性色材)の吸着性に特に優

れるため、好適に用いられる。

【0115】本発明の液体組成物中でのアニオン性微粒子(A)と塩基(B)の混合比率は、質量基準でA:B=200:1~5:1、より好ましくは150:1~8:1の範囲であり、アニオン性微粒子の分散安定性や、該微粒子表面へのカチオン性化合物の吸着性に優れるために好ましい。

【0116】(他の構成成分)次に、アニオン性の液体組成物を構成するその他の成分について具体的に説明する。本発明のアニオン性の液体組成物は、上記したアニオン性微粒子を必須の成分とし、好ましくは上記したような塩基を含み、その他に、通常は液媒体として水を含むが、更に前述のカチオン性液体組成物の項で挙げた有機溶剤及びその他の添加剤、例えば、粘度調整剤、pH調整剤、防腐剤、各種界面活性剤、酸化防止剤、蒸発促進剤、水溶性アニオン性化合物やバインダー樹脂等の添加剤を適宜配合しても構わない。また、後述するように、光重合開始剤や増感剤を液体組成物中に添加することは、モノマーの硬化を効率的に促進させると同時に、液体組成物及びインクの保存安定性において好ましい形態である。

【0117】(液体組成物の表面張力)本発明のアニオン性の液体組成物は、無色或いは白色であるのがより好ましいが、被記録媒体の色に合わせて調色してもよい。更に以上のような液体組成物の各種物性の好適な範囲としては、表面張力を10~60mN/m(dyn/cm)、より好ましくは10~40mN/m(dyn/cm)とし、粘度を1~30mPa・s(cP)としたものである。

【0118】(液体組成物の製造方法)前記のカチオン性又はアニオン性微粒子を含む本発明の液体組成物の製造方法としては、一般に分散に用いられている方法等の中から適宜選択して用いることができる。具体的には、液体組成物中の微粒子の平均粒子径や粒度分布を上記範囲にするために、例えば、ロールミル、サンドミル、ホモジナイザー、超音波ホモジナイザー、超高压乳化機(例えば、商品名ナノマイザー等)等の分散機を用いて分散処理や、遠心分離や限外ろ過等による分級処理等が好適に用いられ、これらの処理手段によって液体組成物中の微粒子の分散粒子径を揃えることができる。

【0119】<水性インク>インク中に含まれる必須成分としてエネルギー付与により重合及び架橋する重合性成分(モノマー)について説明する。

【0120】(重合性成分)本発明におけるインクは、後述する色材の他に必須成分としてエネルギーの付与により架橋重合体に転化する重合性成分(モノマー)及び該モノマーを溶解する溶剤を含有する。該モノマーを用いる目的は、メカニズムの項で述べた通り、プラスチックや金属等の吸液性の乏しい被記録媒体上に着色部を安定に形成させるとともに、着色部を被記録媒体と密

着させて色材を微粒子とともにモノマーへのエネルギー付与により形成された架橋ポリマーで封入することで、着色部の耐擦過性や耐候性を向上させることにある。尚、本発明では、モノマーがエネルギー付与によって重合及び架橋して架橋重合体に転化することを硬化ということがある。

【0121】本発明の液体組成物に用いるエネルギーの付与により硬化するモノマーとしては、ラジカル重合性の(メタ)アクリルモノマー類、カチオン重合システムに適合するエポキシモノマー類が好適に使用できる。ラジカル重合性の(メタ)アクリルモノマー類としては、例えば、下記のモノマーが挙げられる。

【0122】具体的には、

- (1) N, N-ジメチルアミノエチルメタクリレート
 $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
 - (2) N, N-ジメチルアミノエチルアクリレート
 $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
 - (3) N, N-ジメチルアミノプロピルメタクリレート
 $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
 - (4) N, N-ジメチルアミノプロピルアクリレート
 $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
 - (5) N, N-ジメチルアミノアクリルアミド
 $\text{CH}_2=\text{CH}-\text{CON}(\text{CH}_3)_2$
 - (6) N, N-ジメチルアミノメタアクリルアミド
 $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CON}(\text{CH}_3)_2$
 - (7) N, N-ジメチルアミノエチルアクリルアミド
 $\text{CH}_2=\text{CH}-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2$
 - (8) N, N-ジメチルアミノエチルメタアクリルアミド
 $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2$
 - (9) N, N-ジメチルアミノプロピルアクリルアミド
 $\text{CH}_2=\text{CH}-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2$
 - (10) N, N-ジメチルアミノプロピルメタクリルアミド
 $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2$
- 及びこれらの4級化されたモノマー等が色材染着性、皮膜強度に優れており、特に好ましい。

【0123】また、多価アルコールの(メタ)アクリル酸エステル、多価アルコールのグリシジルエーテルの(メタ)アクリル酸エステル、ポリエチレングリコールの(メタ)アクリル酸エステル、多価アルコールのエチレンオキシド付加物の(メタ)アクリル酸エステル、多塩基酸無水物と水酸基含有(メタ)アクリル酸エステルとの反応物等の公知の紫外線硬化型モノマーやオリゴマーが用いられる。これらのモノマーの中から液体組成物中での相溶性や親水性の高い物質が選択されて用いられる。カチオン重合システムに適合するエポキシモノマー類としては、例えば、多価アルコールのグリシジルエーテル、グリシジルエステル、脂肪族環状のエポキシド等

が用いられる。

【0124】本発明において、特にインクに色材として顔料を用いる場合、硬化エネルギーとして紫外線を用いた際に、モノマーの硬化速度は遅くなる傾向にある。従って、紫外線（UV）重合モノマーの重合システムとして、ハイブリット重合システムのモノマーが望ましく、次いで、カチオン重合システム、フリーラジカル重合システムのモノマーを順に選定していくのが望ましい。

【0125】本発明における液体組成物に含有されるモノマーの含有量は、通常 1～50 質量%の範囲が望ましい。1 質量%未満では硬化性が不充分で、生成ポリマーは耐候性、耐溶剤性、耐擦過性、密着性が低いものとなり、50 質量%を越えると組成物の粘度が上昇し、吐出性が悪くなるので好ましくない。好ましくは 3～40 質量%であり、この範囲ではモノマーを選択することで、硬化性と吐出性を両立する液体組成物が得られるという利点があり、更に好ましくは 5～30 質量%であり、この範囲では硬化性は充分であり、吐出性も問題がないのでモノマーの選択性が広がる利点がある。

【0126】（光重合開始剤・増感剤）本発明においてインク中のモノマーの硬化に紫外線エネルギーを用いる場合には、光重合開始剤を用いるのが好ましい。光重合開始剤としては、例えば、カルボニル化合物、アゾ化合物、有機過酸化物等が挙げられる。使用法としては、光重合開始剤を 1 種類又は 2 種類以上使用しても、光重合開始剤と増感剤とを併用しても構わない。主な光重合開始剤と増感剤の選定、組合わせ及び配合比に関しては、使用する紫外線重合性モノマーや使用装置によって適宜選定すればよく、特に制限されない。

【0127】主な光重合開始剤として、例えば、アセトフェノン、2, 2-ジエトキシアセトフェノン、p-ジメチルアミノアセトフェノン、p-ジメチルアミノプロピオフェノン、ベンゾフェノン、2-クロロベンゾフェノン、p, p'-ジクロロベンゾフェノン、p, p'-ビスジエチルアミノベンゾフェノン、ミヒラーケトン、ベンジル（ジフェニルジケトン）、ベンゾイン、ベンゾインメチルエーテル、ベンゾインエチルエーテル、ベンゾインイソプロピルエーテル、ベンゾイン-n-プロピルエーテル、ベンジルジメチルケタール、テトラメチルチウラムモノサルファイド、チオキサンソン、2-クロロチオキサンソン、2-メチルチオキサンソン、アゾビスイソブチロニトリル、ベンゾインパーオキサイド、ジ-tert-ブチルパーオキサイド、1-ヒドロキシシクロヘキシルフェニルケトン、2-ヒドロキシ-2-メチル-1-フェニル-1-オン、1-(4-イソプロピルフェニル)-2-ヒドロキシ-2-メチルプロパン-1-オン、メチルベンゾイルフォーマート等が挙げられる。これらの光重合開始剤の使用量は、通常、紫外線硬化性モノマーの総量に対して 0.1～10

質量%である。

【0128】また、カチオン重合型では、芳香族ジアゾニウム塩、芳香族ハロニウム塩、芳香族スルホニウム塩、メタロセン化合物等の光開始剤が用いられる。その具体例としては、トリフェニルスルフォニウムヘキサフルオロオスフェート、ジフェニルヨードニウムヘキサフルオロアンチモネート等が挙げられる。また、カチオン重合型の場合、硬化を更に完全にするために 80～170℃の範囲で、特に望ましくは 100～150℃の範囲で加熱することが望ましい。加熱時間は、条件により異なるが、通常 5～30 分の間である。

【0129】増感剤としては、例えば、

1. アミン系：脂肪族アミン、芳香族基を含むアミン、ピペリジン、
2. 尿素：アリル系、o-トリルチオ尿素、
3. イオウ化合物：ナトリウムジエチルジチオホスフェート、芳香族スルフィン酸の可溶性塩、
4. ニトリル系化合物：N, N-ジ置換-p-アミノベンゾニトリル、
5. リン化合物：トリ-n-ブチルホスフィン、ネトリウムジエチルジチオホスフィード、
6. 窒素化合物：ミヒラーケトン、N-ニトリソヒドロキシルアミン誘導体、オキサゾリジン化合物、テトラヒドロ-1, 3-オキサジン化合物、ホルムアルデヒド又はアセトアルデヒドとジアミンの縮合物、
7. 塩素化合物：四塩化炭素、ヘキサクロロエタン、
8. エポキシ樹脂とアミンの反応生成物の高分子化アミン、トリエタノールアミントリアクリレート等が挙げられる。

【0130】上記光重合開始剤及び増感剤は、液体組成物又はインクのいずれか一方もしくは両方に含ませることが出来るが、中でもインク側に含ませてモノマーと分離させることにより液体組成物の保存安定性がより一層高くなるために好ましい。硬化エネルギーとして電子線を用いる場合は、上記した光重合開始剤や増感剤は特に必要としない。また、顔料による照射障害もなく温度上昇も少なく硬化速度も速いため、本発明のモノマーの硬化方法としては有効である。

【0131】[アニオン性インク] 次に、上記で説明したカチオン性の液体組成物と組み合わせて本発明のインクセットを構成する水性のアニオン性インクについて説明する。ここでいうインクセットとは、本発明の液体組成物と、アニオン性物質（アニオン性色材）を含有する少なくとも 1 種のアニオン性インクとの組み合わせをいう。また、このインクセットから本発明の液体組成物を除いた、少なくとも 1 種類のインクの組み合わせをインクサブセットと呼ぶ。

【0132】本発明で使用するアニオン性インクは、色材としてアニオン性基を含有する水溶性染料を用いるか或いは色材として顔料を用いる場合には、アニオン性化

化合物を併用させたもの（これも本発明ではアニオン性色材という）を用いることが好ましい。本発明で用いられる上記のようなアニオン性インクには、更にこれに、水、水溶性有機溶剤及びその他の成分、例えば、粘度調整剤、pH調整剤、防腐剤、界面活性剤、酸化防止剤等が必要に応じて含まれて構成される。以下、これらのインクの各構成成分について説明する。

【0133】（水溶性染料）本発明で使用するアニオン性基を有する水溶性染料としては、例えば、カラーインデックス（Color Index：以下ではC. I. と略することがある）に記載されている水溶性の酸性染料、直接染料、反応性染料であれば特に限定されない。また、カラーインデックスに記載のないものでも、アニオン性基、例えば、スルホン基、カルボキシル基等を有するものであれば特に限定されない。ここでいう水溶性染料の中には、溶解度のpH依存性があるものも含まれる。

【0134】（顔料）水性のアニオン性インクの別の形態としては、上記のようなアニオン性基を有する水溶性染料の代わりに、顔料及びアニオン性化合物を用い、水、水溶性有機溶剤及びその他の成分、例えば、粘度調整剤、pH調整剤、防腐剤、界面活性剤、酸化防止剤等を必要に応じて含むインクであってもよい。ここで、アニオン性化合物が顔料の分散剤であってもよいし、顔料の分散剤がアニオン性でない場合に、分散剤とは別のアニオン性化合物を添加したものでもよい。勿論、分散剤がアニオン性化合物である場合でも、更に他のアニオン性化合物を添加したものでもよい。

【0135】本発明で用いることができる顔料には特に限定はないが、例えば、以下に説明する顔料が好適に使用できる。まず、ブラック顔料インクに使用されるカーボンブラックとしては、ファーネス法やチャンネル法で製造されたカーボンブラックで、一次粒径が15～40nm、BET法による比表面積が50～300m²/g、DBP吸油量が40～150ml/100g、揮発分が0.5～10質量%、pH値が2～9を有するものが好ましい。

【0136】このようなものとしては、例えば、No. 2300、No. 900、MCF88、No. 40、No. 52、MA7、MA8、No. 2200B（以上、三菱化学製）：RAVEN 1255（コロンビア製）：REGAL 400R、REGAL 660R、MOGUL L（以上、キャボット製）：Color Black FW1、Color Black FW18、Color Black S 170、Color Black S 150、Printex 35、Printex U（以上、デグッサ製）等の市販品を使用することができる。また、本発明のために新たに試作されたものでもよい。

【0137】イエローインクに使用される顔料としては、例えば、C.I.Pigment Yellow 1、C.I.Pigment Yellow 2、C.I.Pigment Yellow 3、C.I.Pigment Yellow 13、C.I.Pigment Yellow 16、C.I.Pigment Yellow

w 83等が挙げられる。

【0138】マゼンタインクとして使用される顔料としては、例えば、C.I.Pigment Red 5、C.I.Pigment Red 7、C.I.Pigment Red 12、C.I.Pigment Red 48（Ca）、C.I.Pigment Red 48（Mn）、C.I.Pigment Red 57（Ca）、C.I.Pigment Red 112、C.I.Pigment Red 122等が挙げられる。

【0139】シアンインクとして使用される顔料としては、例えば、C.I.Pigment Blue 1、C.I.Pigment Blue 2、C.I.Pigment Blue 3、C.I.Pigment Blue 15：3、C.I.Pigment Blue 16、C.I.Pigment Blue 22、C.I.Vat Blue 4、C.I.Vat Blue 6等が挙げられる。また、上記いずれの色の色材に関しても、本発明のために新たに製造されたものでも使用可能である。

【0140】（顔料分散剤）本発明で使用するインクに用いることができる顔料の分散剤としては、アニオン性基の存在によって、顔料を水、若しくは水性媒体に安定に分散させる機能を有する水溶性樹脂ならどんなものでも使用可能である。特に、重量平均分子量が1,000～30,000の範囲のものが好ましい。更に好ましくは、重量平均分子量が3,000～15,000の範囲である。具体的には、例えば、スチレン、スチレン誘導体、ビニルナフタレン、ビニルナフタレン誘導体、 α 、 β -エチレン性不飽和カルボン酸の脂肪族アルコールエステル等の疎水性単量体、又はアクリル酸、アクリル酸誘導体、マレイン酸、マレイン酸誘導体、イタコン酸、イタコン酸誘導体、フマル酸及びフマル酸誘導体から選ばれた2つ以上の単量体からなるブロック共重合体、グラフト共重合体或いはランダム共重合体、又はこれらの（共）重合体の塩等が挙げられる。これらの樹脂は、塩基を溶解させた水溶液に可溶なアルカリ可溶型の樹脂である。

【0141】更に親水性単量体からなるホモポリマー又はそれらの塩でもよい。また、ポリビニルアルコール、カルボキシメチルセルロース、ナフタレンスルホン酸ホルムアルデヒド縮合物等の水溶性樹脂も使用することも可能である。しかし、アルカリ可溶型の樹脂を用いた場合の方が、分散液の低粘度化が可能で、分散も容易であるという利点がある。前記水溶性樹脂は、インク全量に対して0.1～5質量%の範囲で使用されることが好ましい。

【0142】本発明で用いることができる顔料インクは、以上の如き顔料及び水溶性樹脂を水溶性媒体中に分散又は溶解して構成される。本発明に用いる顔料インクにおいて好適な水性媒体としては、水及び水溶性有機溶剤の混合溶媒であり、水としては種々のイオンを含有する一般の水ではなく、イオン交換水（脱イオン水）を使用するのが好ましい。

【0143】分散剤が、アニオン性高分子ではない場合、上述した顔料を含むインクに更にアニオン性化合物

を添加することが好ましい。本発明で好適に使用されるアニオン性化合物としては、顔料分散剤の項で説明したアルカリ可溶性樹脂等の高分子物質の他、下記に挙げるような低分子量のアニオン性界面活性剤を挙げることができる。

【0144】低分子量のアニオン性界面活性剤の具体的としては、例えば、スルホコハク酸ラウリル二ナトリウム、スルホコハク酸ポリオキシエチレンラウロイルエタノールアミドエステル二ナトリウム、ポリオキシエチレンアルキルスルホコハク酸二ナトリウム、カルボキシル化ポリオキシエチレンラウリルエーテルナトリウム塩、カルボキシル化ポリオキシエチレントリデシルエーテルナトリウム塩、ポリオキシエチレンラウリルエーテル硫酸ナトリウム、ポリオキシエチレンラウリルエーテル硫酸トリエタノールアミン、ポリオキシエチレンアルキルエーテル硫酸ナトリウム、アルキル硫酸ナトリウム、アルキル硫酸トリエタノールアミン等が挙げられるが、これらに限定されるものではない。以上のようなアニオン性物質の好適な使用量は、インク全量に対して、0.05～10質量%の範囲であり、更に好適には0.05～

【0145】（自己分散型顔料）また、アニオン性のインクに用いることのできる顔料としては、分散剤を用いることなしに、水若しくは水性媒体に分散させることのできる自己分散型の顔料も使用できる。自己分散型の顔料は、顔料表面に少なくとも1種のアニオン性親水性基が直接若しくは他の原子団を介して結合されているものである。アニオン性の親水性基としては、例えば、下記に挙げた親水性基の中から選択される少なくとも1種、更に他の原子団が、炭素原子数1～12のアルキレン基、置換基を有してもよいフェニレン基又は置換基を有してもよいナフチレン基等が挙げられる。
 $-COOM$ 、 $-SO_3M$ 、 $-SO_2NH_2$ 、
 $-PO_3HM$ 、 $-PO_3M_2$

（上記式中のMは、水素原子、アルカリ金属、アンモニウム、又は有機アンモニウムを表わす。）

【0146】このように顔料表面への親水性基の導入によってアニオン性に帯電させた顔料は、イオンの反発によって優れた水分散性を有するため、水性インク中に含

アミン或いは塩基の量 (g)

〔樹脂の酸価×アミン或いは塩基の分子量×樹脂量 (g)〕

=

5600

【0151】更に顔料を含む水溶液を分散処理する前にプレミキシングを30分間以上行くと、顔料の分散効率が良い。このプレミキシング操作は、顔料表面の濡れ性を改善し、顔料表面への分散剤の吸着を促進するものである。

【0152】アルカリ可溶性樹脂を使用した場合の分散液に添加される塩基類としては、例えば、モノエタノールアミン、ジエタノールアミン、トリエタノールアミ

有させた場合にも分散剤等を添加しなくても安定した分散状態を維持する。特に顔料がカーボンブラックである場合に好ましい。

【0147】（インク中の添加成分）また、上記の成分の他に、必要に応じて所望の物性値を持つインクとするために、界面活性剤、消泡剤或いは防腐剤等をインク中に添加することができ、更に市販の水溶性染料等を添加することもできる。

【0148】界面活性剤としては、例えば、脂肪酸塩類、高級アルコール硫酸エステル塩類、液体脂肪油硫酸エステル塩類、アルキルアリルスルホン酸塩類等の陰イオン界面活性剤、ポリオキシエチレンアルキルエーテル類、ポリオキシエチレンアルキルエステル類、ポリオキシエチレンソルビタンアルキルエステル類、アセチレンアルコール、アセチレングリコール等の非イオン性界面活性剤が挙げられ、これらの1種又は2種以上を適宜選択して使用できる。その使用量は、分散剤の添加量により異なるが、インク全量に対して、0.01～5質量%が望ましい。この際、インクの表面張力が30mN/m (dyn/cm) 以上になるように界面活性剤の添加量を決定することが好ましい。なぜなら、本発明で使用するインクジェット記録方式においては、ノズル先端の濡れによる印字ヨレ（インク滴の着弾点のズレ）等の発生を有効に抑えることができるからである。

【0149】以上で説明したような顔料インクの作製方法としては、例えば、最初に、顔料分散用樹脂及び水を少なくとも含有する水溶液に、顔料を添加して攪拌した後、後述の分散手段を用いて分散処理を行い、必要に応じて遠心分離処理を行って、所望の分散液を得る。次に、この分散液に上記に掲げたような成分を更に加えて攪拌して、インクとすればよい。

【0150】また、アルカリ可溶性の樹脂を使用する場合には、樹脂を溶解させるために塩基を添加することを要する。この際、樹脂を溶解させるためのアミン或いは塩基の量は、樹脂の酸価から計算によって求められるアミン或いは塩基量の1倍以上を添加することが必要である。アミン或いは塩基の量は、以下の式によって計算で求められる。

ン、アミンメチルプロパノール、アンモニア等の有機アミン或いは水酸化カリウム、水酸化ナトリウム等の無機塩基を用いることが好ましい。

【0153】一方、顔料インクの調製に使用する分散機は、一般に使用される分散機ならいかなるものでもよいが、例えば、ボールミル、サンドミル等が挙げられる。その中でも、高速型のサンドミルが好ましく、例えば、スーパーミル、サンドグライNDER、ピーズミル、アジ

テータミル、グレンミル、ダイノールミル、パールミル、コボルミル（いずれも商品名）等が挙げられる。

【0154】〔カチオン性インク〕次に、先に説明したアニオン性の液体組成物と組み合わせて本発明のインクセットを構成する水性のカチオン性インクについて説明する。ここでいうインクセットとは、本発明の液体組成物とカチオン性物質（カチオン性色材）を含有する少なくとも1種のインクとの組み合わせをいう。また、このインクセットから本発明の液体組成物を除いた、少なくとも1種のインクの組み合わせをインクサブセットと呼ぶ。本発明で使用するカチオン性インクは、色材として、カチオン性基を含有する水溶性染料を用いるか、又は色材として顔料を用いる場合には、カチオン性化合物を併用させること（本発明ではこの併用もカチオン性色材という）が好ましい。本発明で使用される上記のようなインクには、更にこれに、水、水溶性有機溶剤及びその他の成分、例えば、粘度調整剤、pH調整剤、防腐剤、界面活性剤、酸化防止剤等が必要に応じて含まれて構成される。以下、これらのインクの各構成成分について説明する。

【0155】（水溶性染料）本発明で使用するカチオン性基を有する水溶性染料としては、例えば、カラーインデックスに記載されている水溶性の染料であれば特に限定されない。また、カラーインデックスに記載のないものでも、カチオン性基を有するものであれば特に限定はない。尚、ここでいう水溶性染料の中には、溶解度のpH依存性があるものも含まれる。

【0156】（顔料）本発明で使用するインクの別の形態としては、上記したカチオン性基を有する水溶性染料の代わりに、顔料及びカチオン性化合物を用い、水、水溶性有機溶剤及びその他の成分、例えば、粘度調整剤、pH調整剤、防腐剤、界面活性剤或いは酸化防止剤等を必要に応じて含むインクであってもよい。ここで、カチオン性化合物が顔料の分散剤であってもよいし、顔料の分散剤がカチオン性でない場合に、分散剤とは別のカチオン性化合物を添加したのもでもよい。勿論、分散剤がカチオン性化合物である場合でも、更に他のカチオン性化合物を添加してもよい。本発明で使用する顔料としては特に限定はなく、アニオン性インクの項で述べた顔料を好適に用いることができる。

【0157】（顔料分散剤）本発明で使用するインク中の顔料の分散剤は、カチオン性基の存在によって顔料を水、若しくは水性媒体に安定に分散させる機能を有する水溶性樹脂ならどんなものでも使用可能である。具体例としては、ビニルモノマーの重合によって得られるものであって、得られる重合体の少なくとも一部がカチオン性を有するものであればよい。カチオン性の部分を構成するためのカチオン性モノマーとしては、下記の如き第3級アミンモノマーの塩及びこれらの4級化された化合物が挙げられる。

【0158】具体的には、

N, N-ジメチルアミノエチルメタクリレート
 $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]$ 、
 N, N-ジメチルアミノエチルアクリレート
 $[\text{CH}_2=\text{CH}-\text{COO}-\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]$ 、
 N, N-ジメチルアミノプロピルメタクリレート
 $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$ 、
 N, N-ジメチルアミノプロピルアクリレート
 $[\text{CH}_2=\text{CH}-\text{COO}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$ 、
 N, N-ジメチルアクリルアミド
 $[\text{CH}_2=\text{CH}-\text{CON}(\text{CH}_3)_2]$ 、
 N, N-ジメチルメタクリルアミド
 $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{CON}(\text{CH}_3)_2]$ 、
 N, N-ジメチルアミノエチルアクリルアミド
 $[\text{CH}_2=\text{CH}-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2]$ 、
 N, N-ジメチルアミノエチルメタクリルアミド
 $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2]$ 、
 N, N-ジメチルアミノプロピルアクリルアミド
 $[\text{CH}_2=\text{CH}-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$ 、
 N, N-ジメチルアミノプロピルメタクリルアミド
 $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONH}-\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]$
 等が挙げられる。

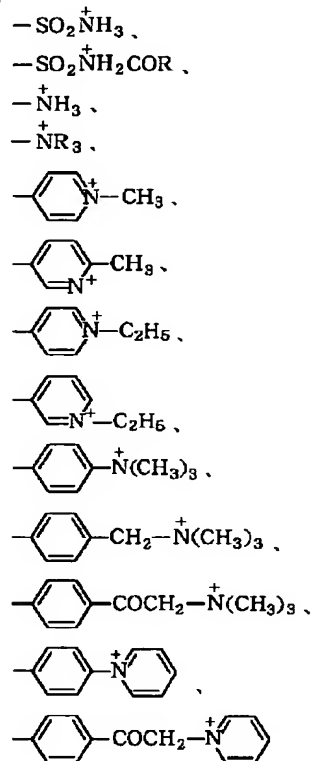
【0159】第3級アミンモノマーの場合において、塩を形成するための化合物としては、例えば、塩酸、硫酸及び酢酸等が挙げられ、4級化に用いられる化合物としては、例えば、塩化メチル、ジメチル硫酸、ベンジルクロライド、エピクロロヒドリン等が挙げられる。これらの中でも、塩化メチルやジメチル硫酸等が本発明で使用する分散剤を調製するうえで好ましい。以上のような第3級アミンモノマーの塩或いは第4級アンモニウム化合物は水中ではカチオンとして振る舞い、中和された条件では酸性が安定溶解領域である。これらモノマーの共重合体中での含有率は20～60質量%の範囲が好ましい。

【0160】上記高分子分散剤の構成に用いられるその他モノマーとしては、例えば、2-ヒドロキシエチルメタクリレート、長鎖のエチレンオキシド鎖を側鎖に有するアクリル酸エステル等のヒドロキシ基を有するアクリル酸エステル、スチレン系モノマー等の疎水性モノマー類及びpH7近傍の水に溶解可能な水溶性モノマーとして、アクリルアミド類、ビニルエーテル類、ビニルピロリドン類、ビニルピリジン類、ビニルオキサゾリン類が挙げられる。疎水性モノマーとしては、スチレン、スチレン誘導体、ビニルナフタレン、ビニルナフタレン誘導体、（メタ）アクリル酸のアルキルエステル、アクリロニトリル等の疎水性モノマーが用いられる。共重合によって得られる高分子分散剤において水溶性モノマーは、共重合体を水溶液中で安定に存在させるために15～35質量%の範囲で用い、且つ疎水性モノマーは、共重合体の顔料に対する分散効果を高めるために20～4

0質量%の範囲で用いることが好ましい。

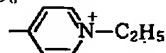
【0161】（自己分散型顔料）カチオン性に帯電した顔料の場合、直接若しくは他の原子団を介して結合した親水性基が、例えば、下記に挙げる第4級アンモニウム基から選ばれる少なくとも1つを結合したものが挙げられる。しかし、本発明はこれらに限定されるものではない。

【0162】



【0163】上記式中、Rは炭素原子数1～12の直鎖状又は分岐鎖状のアルキル基、置換若しくは未置換のフェニル基、又は置換若しくは未置換のナフチル基を表す。尚、上記のカチオン性基には、カウンターイオンとして、例えば、 NO_3^- や CH_3COO^- が存在する。

【0164】上記したような親水性基が結合されてカチオン性に帯電している自己分散型顔料を製造する方法としては、例えば、下記に示す構造のN-エチルピリジル基を結合させる方法を例にとりて説明すると、顔料を3-アミノ-N-エチルピリジニウムブロマイドで処理する方法が挙げられる。



【0165】このように顔料表面への親水性基の導入によってカチオン性に帯電させた顔料は、イオンの反発によって優れた水分散性を有するため、水性インク中に含有させた場合にも分散剤等を添加しなくても安定した分散状態を維持する。特に上記顔料がカーボンブラックである場合が好ましい。

【0166】（インクの表面張力）更に本発明で使用するカチオン性インクは被記録媒体へのインクの浸透性や濡れと同時に、インクジェット用ヘッドに対するマッチングを良好にする面から、前記界面活性剤を添加することで、インク自体の物性として25℃における表面張力が30～68mN/m (dyn/cm)、粘度が15mPa·s (cP) 以下、好ましくは10mPa·s (cP) 以下、より好ましくは5mPa·s (cP) 以下に調整されることが望ましい。

10 【0167】（インク中に含まれる他の成分）尚、本発明で使用するインクは、上記成分の他に必要に応じて、水溶性有機溶剤、界面活性剤、pH調剤、防錆剤、防カビ剤、酸化防止剤、蒸発促進剤、キレート化剤及び水溶性ポリマー等の添加剤を添加してもよい。

【0168】本発明で用いることのできる上記モノマーを溶解又は分散する液媒体は、水と水溶性有機溶剤との混合物であることが好ましい。具体的水溶性有機溶剤としては、例えば、メチルアルコール、エチルアルコール、n-プロピルアルコール、イソプロピルアルコール、n-ブチルアルコール、sec-ブチルアルコール、tert-ブチルアルコール等の炭素数1～4のアルキルアルコール類：ジメチルホルムアミド、ジメチルアセトアミド等のアミド類：アセトン等のケトン類：テトラヒドロフラン、ジオキサン等のエーテル類：ポリエチレングリコール、ポリプロピレングリコール等のポリアルキレングリコール類：エチレングリコール、プロピレングリコール、ブチレングリコール、トリエチレングリコール、1, 2, 6-ヘキサントリオール、チオジグリコール、ヘキシレングリコール、ジエチレングリコール等のアルキレン基が2～6個の炭素原子を含むアルキレングリコール類：グリセリン、エチレングリコールモノメチル（又はエチル）エーテル、ジエチレングリコールモノメチル（又はエチル）エーテル等の多価アルコールの低級アルキルエーテル類：N-メチル-2-ピロリドン、1, 3-ジメチル-2-イミダゾリジノン、スルホラン、ジメチルスルフォキシド、2-ピロリドン、ε-カプロラクタム等の環状アミド化合物及びスクシンイミド等のイミド化合物等が挙げられる。

40 【0169】上記水溶性有機溶剤の含有量は、一般には、インクの全質量に対して1～40%が好ましく、より好ましくは3～30%の範囲である。また、インク中の水の含有量は、例えば、30～95質量%の範囲とした場合、色材の溶解性等も良好であり、インクの粘度が高くなることを抑えることができ、且つ固着特性を十分に満足させることができるので好ましい。

50 【0170】本発明で使用するインクは、一般の水性筆記用具のインクとしても使用できるが、熱エネルギーによるインクの発泡現象によりインクを吐出させるタイプのインクジェット記録方法に適用する場合に特に好適であり、吐出が極めて安定となり、サテライトドットの発

生等が生じないという特徴がある。但し、この場合には、熱的な物性値（例えば、比熱、熱膨張係数、熱伝導率）を調整する場合もある。

【0171】＜水性インクの濃度＞上記したアニオン性及びカチオン性のインク中に含まれる色材成分の濃度は、水性染料、顔料や自己分散型顔料等の色材の種類に応じて適宜選択されるが、インクの全質量に対し、0.1～20%、特に0.1～12%の範囲が好ましい。また、色材成分の濃度が0.3～7質量%の範囲では、液体組成物中の微粒子の濃度とインク中の色材の濃度との関係に関して、質量基準で、該微粒子1に対して色材が1.2以下、特に1.0以下とした場合、通常の2液系の記録条件の下で形成される画像の発色性は特に優れたものとなる。

【0172】＜被記録媒体に着色部を形成する方法＞次に、本発明の被記録媒体に着色部を形成する方法について説明する。本発明の被記録媒体に着色部を形成する方法は、(i) 色材及びエネルギーの付与によって重合するモノマー及び該モノマーを溶解する溶剤を含む、アニオン性若しくはカチオン性のインクを被記録媒体に付与する過程及び(ii) 該インクとは逆の極性に表面が帯電している微粒子を分散状態で含む液体組成物を被記録媒体に付与する過程とを有し、インクと液体組成物とを互いに液体状態で接するように上記被記録媒体の表面に付与することを特徴とする。以下、上述したように構成されている液体組成物及びインクを被記録媒体上に付与する方法について説明する。

【0173】本発明の被記録媒体に着色部を形成する方法は、上記で説明したような液体組成物を被記録媒体上に付与する過程(ii)と、色材及びエネルギーの付与によって重合するモノマー及び該モノマーを溶解する溶剤を含む、アニオン性若しくはカチオン性のインクを被記録媒体に付与する過程(i)を含む。その際に、色材を含むインクによって形成される被記録媒体の着色部形成領域、又は着色部形成領域とその近傍に液体組成物を付与するが、インクと液体組成物を、それらが互いに液体状態で接するように付与する。ここでいう着色部形成領域とは、インクのドットが付着する領域のことであり、着色部形成領域の近傍とは、インクのドットが付着する領域の外側の1～5ドット程度離れた領域のことを指す。

【0174】本発明の被記録媒体に着色部を形成する方法では、前記した本発明の液体組成物とインクとが被記録媒体上で互いに液体状態で接するようになる方法であれば、これらをいずれの方法で付与させてもよい。従って、液体組成物とインクのいずれを先に被記録媒体上に付与するかは問題ではない。例えば、過程(ii)を行なった後に過程(i)を行なってもよいし、過程(i)を行なった後に過程(ii)を行なってもよい。また、過程(i)を行なった後に、過程(ii)を行ない、その後

再び過程(i)を行なうことも好ましい。また、液体組成物を被記録媒体に先に付与させた場合に、液体組成物を被記録媒体に付与してから、インクを被記録媒体上に付与させるまでの時間については特に制限されるものではないが、互いに液体状態で接するようにするためには、ほぼ同時或いは数秒以内にインクを被記録媒体上に付与させることが好ましい。

【0175】次に、インク中のモノマーを硬化させるエネルギーを与えるタイミングについても、インクと液体組成物の双方を付与した後であればいつでも自由に選択し得る。但し、最後の液体組成物の画素を形成した後は必ずエネルギーを与えモノマーを硬化する必要がある。また、液体組成物及びインク中の溶剤の除去、即ち、乾燥についてはエネルギーを与える時には殆どの溶剤が除去されていることが好ましい。乾燥手段としては、基材（被記録媒体）を50～200℃程度の温度の熱風炉に入れるのが好ましい。但し処理時間の短縮の目的から溶剤の除去を完全に行なわない状態でモノマーの重合等を行ない、後で乾燥を行なってもよい。いずれにしても、最終画像形成物においては溶剤が残っているのは画像物性の良いものが得られないので好ましくない。また、モノマーを硬化する手段としてのエネルギー付与は、前述のように紫外線照射、電子線照射、熱線照射等が挙げられる。例えば、紫外線照射手段としては、高圧水銀灯を用いて積算で200～1000 mJ/cm²程度の紫外線を照射するのが好ましい。上記高圧水銀灯の水銀ランプの紫外線領域の発光スペクトルは、184 nm～450 nmの範囲であり、紫外線硬化性モノマーを効率的に硬化させるのに適している。また、電子線照射装置を用いる場合には1～50 Mradの範囲で照射を行うのが好ましい。

【0176】（被記録媒体）上記した本発明の被記録媒体に着色部を形成する方法に使用される被記録媒体は、特に限定されるものではなく、例えば、印刷用のアート紙やプラスチック、金属、タイル等、吸液性の乏しい材質のものや、従来から使用されているコピー用紙、ボンド紙等のいわゆる普通紙等、様々な物が好適に使用される。勿論、インクジェット記録用に特別に作製されたコート紙やOHP用透明フィルムも好適に使用される。更に一般の上質紙や光沢紙も好適に使用することができる。

【0177】（液体組成物の付与方法）本発明の液体組成物を被記録媒体上に付与せしめる方法としては、例えば、スプレーやローラー等によって被記録媒体の全面に付与せしめる方法も考えられるが、更に好ましくはインクを付与する着色部形成領域、或いは着色部形成領域とその着色部形成領域の近傍にのみに選択的、且つ均一に液体組成物を付与せしめることのできるインクジェット方式により行うのが好ましい。また、この際には、種々のインクジェット記録方式を用いることができるが、特

に好ましいのは熱エネルギーによって発生した気泡を用いて液滴を吐出する方式である。

【0178】＜インクジェット記録装置＞次に、本発明のインクジェット記録装置について説明する。本発明のインクジェット記録装置は、色材及びエネルギーの付与によって重合するモノマー及び該モノマーを溶解する溶剤を含む、アニオン性若しくはカチオン性の水性インクを収容したインク収容部と、該インクを吐出させるインクジェットヘッドを備えた第1の記録ユニットと、前記本発明の液体組成物を収容した液体組成物収容部と、該液体組成物を吐出させるインクジェットヘッドを備えた第2の記録ユニットとを備えていることを特徴とする。

【0179】特に本発明のインクジェット記録方法に用い得るインクジェット記録装置は、インク吸収性のない被記録媒体に対してもインク吐出口を複数備えた記録ヘッドから液体組成物及び少なくとも1色以上のインクを付与して記録画像を形成するインクジェット記録装置であって、

- a) 前記被記録媒体表面を清浄化処理する手段と、
- b) 画像記録信号に応じてインク滴を飛翔させ、前記被記録媒体表面の所定位置にインク滴を付与するインク吐出口を複数備えた記録ヘッドと、
- c) 前記画像形成のインク滴を硬化させる手段とを具備する。

【0180】本発明に係るインクジェット記録装置において、a) の手段は、被記録媒体によっては省略しても構わない。また、手法としては、例えば、UV/O₃洗浄が挙げられる。c) のインク滴の硬化手段としては、UV照射ランプ、EB（電子線）照射、熱等が挙げられる。UV照射ランプにおいては、熱が発生し被記録媒体が変形してしまう可能性があるため、冷却機構、例えばコールドミラー、コールドフィルター、ワーク冷却等が具備されていることが好ましい。

【0181】図1は、インクジェット記録装置全体を示す模式的概略図である。図1中の110は記録ヘッドで、600dpiの300ノズル×5列が一体に並んで配列されたインクジェット記録ヘッドである。上記記録ヘッドは液体組成物及びインクとして、Y（イエロー）、M（マゼンタ）、C（シアン）及びBk（ブラック）の4色分用の5つのヘッドが設けられ、一走査でフルカラーの画像を記録できるようにセットされている。101は被記録媒体である。ストッカー111に複数枚の被記録媒体101がセットされており、搬送機112によりベルトコンベアー113に送られ、印字用トレー115に送り出される。114は被記録媒体を送るための補助ローラである。

【0182】印字用トレー115に送られた被記録媒体101は、ポンプ116での吸引によりトレー上にしっかりと吸着固定される。印字用トレー115上の被記録媒体101が第1の処理過程が行われる領域に送り込ま

れる。104はUV/O₃ランプである。被記録媒体によって表面の濡れ性が低い場合は、被記録媒体の表面処理を行い、インクの濡れ性や密着性を向上させる。この処理過程はパス（省略）してもかまわない。

【0183】111の送りモータで第1の過程の領域から被記録媒体が搬出されると、直ちに記録ヘッド110によるインクジェット記録が行われる。この第2の過程であるインクジェット記録には、ピエゾ方式や静電方式等、種々のインクジェット記録方式が利用できるが、高速記録を安定して行うことのできるバブルジェット（登録商標）方式が好適である。

【0184】また、記録方法としても、1パス印字の場合に滲み等の問題が発生するようであれば、2パスや4パス印字が採用される。画像が記録された被記録媒体は、第3の過程の固化処理が行われる領域に直ちに搬送される。ここで、105はUV照射ランプである。

【0185】UVランプの照射によって熱が発生し、被記録媒体の変形を起こす可能性があるため、コールドミラー、コールドフィルター、ワーク空冷（以上図中不図示）等の加熱防止機構が必要である。

【0186】以上の3つの処理過程を経た被記録媒体（記録画像を有する）は、ベルトコンベアー120と送りローラ121を介してストッカー119に搬送され、ハンドラー118によって所定位置に収納される。

【0187】図示した例においては、被記録媒体101は板形状のものであるが、これを搬送するトレーは被記録媒体の形状に対応できるように適宜調節される。例えば、図3に示すようなスペーサー211等を用いることで円盤状の被記録媒体101への記録にも対応可能となる。また、この装置は被記録媒体の厚みに応じて記録ヘッドと被記録媒体の画像形成面との距離を調整する手段を有していることが望ましい。

【0188】また、第1の過程や第3の過程における加熱硬化（重合体の架橋）を促進するためには、トレーにヒーター等の加熱手段を補助的に設けて、例えば、被記録媒体を各処理前に加熱しておくことで、熱容量の大きな比較的大型の被記録媒体の処理にでも加熱効率を高めて効果的な処理が可能となる。

【0189】尚、被記録媒体に加熱処理を行った際に、熱膨張によって寸法に狂いが生じ、記録の幅方向及び送り方向のずれが生じ、記録画像での白スジの発生や印字サイズのズレ等の問題が起る場合には、例えば、図4に示すように、被記録媒体401の画像形成面の表面温度を温度センサー402で検知し、増幅器（Amp）で増幅し、これをA/Dコンバーター（A/D）でデジタル化してからコンパレータで予め設定された値と比較して、クロックの信号に対する最適ディレー信号で記録ヘッド410とモータ403へ信号を送り、正しい位置に被記録媒体をセットできるように調整するシステムを用いるのが好ましい。

【0190】また、被記録媒体を精度よく搬送させるために、被記録媒体の非印字領域にエッチングやプレスによって目印をマーキングし、その位置を適当な読取り手段で読取り、被記録媒体の位置を常に確認し、その位置によって搬送手段を制御してより精度よい搬送を行うこともできる。また、被記録媒体に反り等がある場合には、反り等の補正のためにローラ等に反りを矯正する機能を付加しておくことも有効である。また、前記の目印が製品価値を損なうものであれば、印字後にシャーリングプレス等の手段によりこれを取り除けばよい。

【0191】図2は、他の記録装置全体を示す模式的概略図である。図中130は、インクの各色毎に液体組成物を付与したタイプの記録ヘッドで、例えば600dpi 300×2列のインクジェット記録ヘッドである。130Y、130M、130C及び130BはY（イエロー）、M（マゼンタ）、C（シアン）及びB（ブラック）の各1色及び液体組成物を1セットにした記録ヘッドである。例えば、130Yでイエロー及び液体組成物を印字した後、105のUVランプによりUV照射を行い、少なくともインクの表面が硬化するだけのUVを照射する。

【0192】111の送りモータで、搬送トレイ115上の被記録媒体101は次の色の印字を行うため、次の130Mのインクジェット記録ヘッドのところへ搬送される。印字後、UVランプ105により、インク表面を硬化させる。続いて130C、130Bとくり返して、フルカラーの画像が形成される。その他の詳細な説明は図1の説明と同様である。

【0193】図1及び図2は、1色又は4色印字後にUV照射を行っているが、インクカートリッジ横にスポットUVランプを設置し、1パス毎にUV照射してもかまわない（不図示）。

【0194】

【実施例】次に、実施例及び比較例を挙げて本発明を更に具体的に説明する。尚、文中、「部」及び「%」とあるのは特に断りのない限り質量基準である。

【0195】まず、本発明の液体組成物の作製について説明する。以下に示す各成分を混合溶解した後、ポアサイズが1μmのメンブレンフィルター（商品名、フロロポアフィルター、住友電工（株）製）にて加圧濾過し、本発明の液体組成物A～Cを得た。

【0196】（アルミナ水和物の合成例）米国特許明細書第4,242,271号に記載の方法でアルミニウムドデキシドを製造した。次に、米国特許明細書第4,202,870号に記載された方法で、前記アルミニウムドデキシドを加水分解してアルミナスラリーを製造した。このアルミナスラリーをアルミナ水和物の固形分が8.2%になるまで水を加えた。アルミナスラリーのpHは9.7であった。3.9%の硝酸溶液を加えてpHを5.3に調整し、オートクレーブにて120度で7時

間熟成させてコロイダルゾルを得た。このコロイダルゾルを硝酸でpH=4.0に調整し、固形分濃度20%に濃縮してアルミナ水和物スラリーを作製した。このスラリー中のアルミナ水和物は水中で表面がプラスに帯電し、カチオン性を示す。また、このアルミナ水和物スラリーをイオン交換水に希釈し分散させてコロジオン膜上に滴下して測定用試料を作製し、透過型電子顕微鏡で観察したところ平板形状の微粒子であった。

【0197】＜液体組成物Aの組成＞

・グリセリン	10.0部
・ジエチレングリコール	7.5部
・アルミナ水和物スラリー	50.0部
・水	32.5部

上記成分を乳化分散機（TKロボミックス、特殊機化工業（株）製）にて3000rpmで30分間混合した後、遠心分離処理（4000rpm、15分間）を行い、粗大粒子を除去して液体組成物Aとした。

【0198】 ＜液体組成物Bの組成＞

・1.5-ペンタンジオール	10.0部
・エチレングリコール	7.5部
・コロイダルジルコニアゾル（固形分濃度20%）	50.0部
・水	32.5部

上記成分を乳化分散機（TKロボミックス、特殊機化工業（株）製）にて3000rpmで30分間混合した後、遠心分離処理（4000rpm、15分間）を行い、粗大粒子を除去して液体組成物Bとした。このジルコニアゾル中のジルコニア微粒子は水中で表面がプラスに帯電し、カチオン性を示す。

【0199】＜液体組成物Cの組成＞

・グリセリン	10.0部
・ジエチレングリコール	7.5部
・アルミナ水和物スラリー	50.0部
・光重合開始剤（IRGACURE 2959、チバガイギー社製）	3.0部
・水	29.5部

上記成分を乳化分散機（TKロボミックス、特殊機化工業（株）製）にて3000rpmで30分間混合した後、遠心分離処理（4000rpm、15分間）を行い、粗大粒子を除去して液体組成物Cとした。

【0200】上記液体組成物A～Cを下記の方法により測定を行い、各々の特性及び評価結果を表1に示した。

1) 微粒子の平均粒子径

微粒子の固形分濃度を0.1%になるよう液体組成物をイオン交換水で希釈した後、超音波洗浄機にて5分間分散させて、電気泳動光散乱光度計（大塚電子（株）社製、ELS-8000：液温25℃、石英セル使用）を用いて散乱強度を測定した。平均粒子径は付属のソフトウェアを用い、散乱強度からキュムラント解析法により

求めた。

【0201】2) pH

液体組成物に対し、液温 25℃で pHメーター計（堀場製作所（株）製、カスタニー pHメーター D-14）を用いて測定した。

3) ゼータ電位

微粒子の固形分濃度が 0.1%になるよう液体組成物をイオン交換水で希釈した後に、ゼータ電位測定機（ブルックヘブン社製、BI-ZETA plus：液温 20℃、アクリルセル使用）で測定した。

【0202】4) タンク保存性

液体組成物をインクタンクに詰め、60℃の恒温槽に1ヶ月間静置保存し、タンク内の液体組成物の液物性及び記録ヘッドからの吐出性を評価した。

○：タンク内でほぼ沈降が見られず、吐出安定性も良好。

×：タンク内で著しく沈降し、吐出性も不安定。

【0203】

表1

液体組成物	A	B	C
平均粒子径 (nm)	70	115	75
pH	4.1	3.9	3.8
ゼータ電位 (mV)	41	69	40
タンク保存性	○	○	○

【0204】次に、本発明の実施例及び比較例で使用するインクサブセット1、2の作製について説明する。

＜インクサブセット1の作製＞下記に示す各成分を混合し、十分攪拌して溶解後、ポアサイズが 0.45 μm のフロロポアフィルター（商品名、住友電工（株）製）にて加圧濾過し、ブラック、イエロー、マゼンタ及びシアンの各染料インク、Bk1、Y1、M1及びC1を得、これらの染料インクからなる組み合わせをインクサブセット1とした。

【0205】[ブラックインク Bk1]

・ C. I. ダイレクトブラック 195	2.5部
・ 2-ピロリドン	10.0部
・ グリセリン	5.0部
・ イソプロピルアルコール	4.0部
・ 水酸化ナトリウム	0.4部
・ アクリルモノマー (*1)	10.0部
・ 水	68.1部

【0206】[イエローインク Y1]

・ Projet Fast Yellow 2 (Zeneca社製)	2.0部
・ C. I. ダイレクトイエロー 86	1.0部
・ チオジグリコール	8.0部
・ エチレングリコール	8.0部
・ アセチレノール EH	0.2部
(川研ケミカル社製)	

・ イソプロピルアルコール	4.0部
・ アクリルモノマー (*1)	10.0部
・ 水	66.8部

【0207】[マゼンタインク M1]

・ Projet Fast Magenta 2 (Zeneca社製)	3.0部
・ グリセリン	7.0部
・ 尿素	7.0部
・ アセチレノール EH	0.2部
(川研ケミカル社製)	

10	・ イソプロピルアルコール	4.0部
	・ アクリルモノマー (*1)	10.0部
	・ 水	68.8部

【0208】[シアンインク C1]

・ C. I. ダイレクトブルー 199	3.0部
・ エチレングリコール	7.0部
・ ジエチレングリコール	10.0部
・ アセチレノール EH	0.3部
(川研ケミカル社製)	

20	・ アクリルモノマー (*1)	10.0部
	・ 水	69.7部

(注) *1：エトキシ化トリメチロールプロパントリ
アクリレート

(商品名 A-TMPT-3EO、新中村化学（株）製)

【0209】＜インクサブセット2の作製＞下記に示す各成分によって顔料分散液を調製し、これを用いてブラックインク Bk2 を作製した。更に同様の顔料分散液を用いてイエロー、マゼンタ及びシアンの各顔料インク、Y2、M2及びC2を得、これらの顔料インクからなる組み合わせをインクサブセット2とした。

30 【0210】[ブラックインク Bk2]

(顔料分散液の作製)

・ スチレン-アクリル酸-アクリル酸エチル共重合体 (酸価 140、重量平均分子量 5,000)	1.5部
・ モノエタノールアミン	1.0部
・ ジエチレングリコール	5.0部
・ 水	81.5部

【0211】上記成分を混合し、ウォーターバスで 70℃に加熱し、樹脂分を完全に溶解させる。この溶液に新たに試作されたカーボンブラック (MCF88、三菱化学製) 10部、イソプロピルアルコール 1部を加え、30分間プレミキシングを行った後、下記の条件で分散処理を行った。

・ 分散機：サンドグラインダー (五十嵐機械製)
・ 粉碎メディア：ジルコニウムビーズ、1mm径
・ 粉碎メディアの充填率：50% (体積比)
・ 粉碎時間：3時間

更に遠心分離処理 (12,000rpm、20分間) を行い、粗大粒子を除去して分散液とした。

50 【0212】(ブラックインク Bk2の作製) 上記の顔料分散液を使用し、下記の組成比を有する成分を混合

し、顔料を含有するインクを作製し、これをブラックインク B k 2 とした。

- ・上記顔料分散液 30.0部
- ・グリセリン 10.0部
- ・エチレングリコール 5.0部
- ・N-メチルピロリドン 5.0部
- ・エチルアルコール 2.0部
- ・アクリルモノマー 10.0部

(商品名NKエステルA-200、新中村化学(株)製)

- ・水 38.0部

【0213】[イエローインクY2]ブラックインク B k 2 の調製の際に使用したカーボンブラック(MCF88、三菱化学製)10部を、ピグメントイエロー74に代えたこと以外はブラックインク B k 2 の調製と同様に

して、顔料含有イエローインクY2を調製した。
【0214】[マゼンタインクM2]ブラックインク B k 2 の調製の際に使用したカーボンブラック(MCF88、三菱化学製)10質量部を、ピグメントレッド7に代えたこと以外はブラックインク B k 2 の調製と同様に

して、顔料含有マゼンタインクM2を調製した。
【0215】[シアンインクC2]ブラックインク B k 2 の調製の際に使用したカーボンブラック(MCF88、三菱化学製)10質量部を、ピグメントブルー15に代えたこと以外はブラックインク B k 2 の調製と同様に

にして、顔料含有シアンインクC2を調製した。
【0216】(実施例1～実施例6)上記のようにして得られた本発明の液体組成物A～Cと、インクサブセット1、2の各色インクを用いて、下記の表2の組み合わせで印字を行った。尚、実施例1～4までは印字後60℃で5分間乾燥後、直ちに電子線照射を行った。照射条件は電流:6mA、ラインスピード:10m/分、線量:3Mradで行った。一方、実施例5、6は印字後60℃で5分間乾燥後、直ちに紫外線照射を行った。照射量は10J/cm²で行った。これを本発明の実施例1～6とした。

【0217】

表2

実施例	インクサブセット	液体組成物
1	1	A
2	2	A
3	1	B
4	2	B
5	1	C
6	2	C

【0218】上記のようにして液体組成物A～Cとインクサブセット1、2を組み合わせ使用する実施例1～

6の着色部の形成方法においては、100μm厚みのPETフィルムに記録を行った。また、その際に使用したインクジェット記録装置としては、図1に示した記録装置を用いてカラー画像を形成した。この際、液体組成物を先打ちして先ずフィルム上に付着させ、その後、インクを付着させた。印字直後、上記条件でエネルギーを付与して記録画像を硬化させ、定着させた。いずれの実施例も十分硬化していることを確認した。

【0219】具体的には、評価項目(1)～(5)までは印字領域を3回の走査で印字する3パスファイン印字を行った。このとき、液体組成物は各パス毎にイエロー、マゼンタ、シアン及びブラックのいずれかのインクが印字される画素位置に印字を行った。即ち、各パス毎のイエロー、マゼンタ、シアン及びブラックの印字データの論理和を液体組成物の印字データとして用いた。尚、該ファイン印字時のファインマスクの種類には、特に制限はなく、公知の技術が利用可能であるので、こ

この詳細な説明は省略する。
【0220】ここで用いた記録ヘッドは、600dpiの記録密度を有し、駆動条件としては、駆動周波数9.6kHzとした。600dpiのヘッドを使用したときの1ドット当たりの吐出量はイエロー、マゼンタ、シアンインク及び液体組成物については夫々15ng、ブラックインクについては1ドット当たり30ngのヘッドを使用した。尚、これらの記録条件は、実施例及び参考例を通じて同一である。

【0221】(参考例1、2)上記のようにして得られたインクサブセット1、2の各色インクのみを用いて、下記の表3の組み合わせで印字を行った。尚、参考例1、2は印字後60℃で5分間乾燥後、直ちに電子線照射を行った。照射条件は電流:6mA、ラインスピード:10m/分、線量:3Mradで行った。

【0222】

表3

参考例	インクサブセット	液体組成物
1	1	なし
2	2	なし

【0223】上記液体組成物C及びインクサブセット1、2を用いた記録(参考例1～2)において用いた記録ヘッドは、600dpiの記録密度を有し、駆動条件としては、駆動周波数9.6kHzとした。600dpiのヘッドを使用したときの1ドット当たりの吐出量は、イエロー、マゼンタ及びシアンインクについては夫々約15ng、ブラックインクについては1ドット当たり約30ngのヘッドを使用し、実施例1～6の場合と同条件で記録を行った。

【0224】[評価方法及び評価基準]上記の実施例1～6及び参考例1、2で得られた夫々の記録画像につい

て、下記の評価方法及び評価基準で評価を行った。その結果を表4に示した。

【0225】（記録画像の評価方法）

（1）発色性

高精細XYZ・CIELAB・RGB標準画像（SHIPP）（監修：高精細標準画像作成委員会：画像電子学会発行）のRGBカラーチャートをプリンタを用いて印字し、それらのカラーチャートを測色した。発色性の評価は同技術解説書に記載されている方法で色彩分布の3次元的な広がり

（以下、文中では色域体積と呼ぶ）の計算を行い、比較した。その際、印字画像を形成する際の画像処理は同一条件とし、測色は、印字後24時間経過後、GRETAGスペクトロリノで光源：D50、視野：2°の条件で測定した。その評価基準を以下に示した。参考例1に対しての実施例1及び2、参考例2に対しての実施例3及び4、参考例3に対しての実施例5及び6の各々の色域体積の比を、評価基準とした。

【0226】AA：色域体積比が1.4倍以上。

A：色域体積比が1.2～1.4倍未満。

B：色域体積比が1.0～1.2倍未満。

C：色域体積比が1.0倍未満。

【0227】（2）均一性

前記したプリンタを用いて、イエロー、マゼンタ、シアン及びブラック各色のベタ画像を印字した後、目視にて、白モヤと色ムラに関して色の均一性を評価した。特に均一性の悪い色を評価対象とした。評価基準は、以下の通りである。

A：白モヤや色ムラは殆ど発生しない。

B：若干紙の繊維に沿って白モヤや色ムラが見えるが、実質上問題のないレベルである。

C：紙の繊維に沿って著しく白モヤや色ムラが見える。

【0228】（3）スジムラ

前記したプリンタを用いて、イエロー、マゼンタ、シアン及びブラック各色のベタ画像を印字した後、目視にて、スジムラを評価した。特にスジムラの悪い色を評価対象とした。評価基準は以下の通りである。

A：スジムラは殆ど発生しない。

B：若干ヘッドスキャン毎のスジムラが見えるが、実質上問題のないレベルである。

C：著しくヘッドスキャン毎の白いスジムラが見える。

【0229】（4）耐擦過性

前記したプリンタを用いて、イエロー、マゼンタ、シアン及びブラック各色のインクのベタ画像を印字した。印字して16時間後、記録画像の鉛筆硬度をJIS-K5400に準じて測定した。最も硬度の低いものを評価対象とした。

【0230】（5）耐候性

前記したプリンタを用いて、イエロー、マゼンタ、シアン及びブラック各色のインクのベタ画像を印字した。印字して24時間後、記録画像をオゾンウェザーメータ

ー（スガ試験機社製）にて槽内温度40℃、槽内湿度55%、オゾン濃度3ppm、暴露時間2時間の条件で暴露試験を行った。試験前後の各色のΔEを測定し、最も色味変化の著しいものを評価対象として下記基準にて評価した。

A：ΔEが5未満。

B：ΔEが5～10未満。

C：ΔEが10以上。

【0231】

表4

	発色性	均一性	スジムラ	耐擦過性	耐候性
実施例1	AA	A	A	4H	A
実施例2	AA	A	A	4H	A
実施例3	A	A	A	4H	A
実施例4	A	A	A	4H	A
実施例5	AA	A	A	4H	A
実施例6	AA	A	A	4H	A
参考例1	B	B	B	4H	A
参考例2	B	B	B	4H	A

【0232】

【発明の効果】以上説明したように、本発明によれば、特に、プラスチックや金属等の吸液性の乏しい被記録媒体に対しても、インクジェット用コート紙並みの優れた発色性と色の均一性が得ることができ、ベタ画像部のスジムラが少なく、記録画像の耐擦過性にも優れたインクジェット記録画像が得られ、且つ保存性や印字における信頼性、具体的には記録ヘッドからの吐出安定性や目詰まりを生じない等の信頼性にも優れるインクセット、被記録媒体に着色部を形成する方法及びインクジェット記録装置が提供される。

【図面の簡単な説明】

【図1】 本発明のインクジェット記録装置の1例の要部を示す模式的概略図。

【図2】 本発明のインクジェット記録装置の他の例を示す模式的概略図。

【図3】 本発明のインクジェット記録装置に用いるトレーの構成例を示す説明図。

【図4】 本発明のインクジェット記録装置における被記録材と記録ヘッドの位置合わせの際の被記録材の画像形成面の温度に応じた位置補正システムの1例を示す図である。

【図5】 コート紙にインクジェット記録を行なったときの着色部の状態を説明する模式的断面図。

【図6】 本発明にかかるインクジェット画像の着色部の状態を説明する模式的断面図。

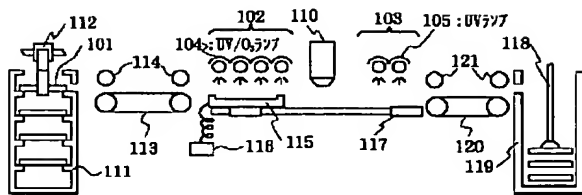
【図7】 本発明にかかるインクジェット記録画像の着色部の形成過程を示す概略過程図。

【符号の説明】

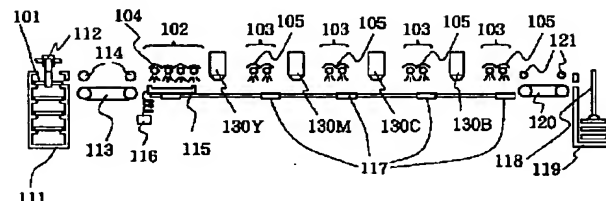
101 : 被記録媒体
 102 : 第1の過程が行われる領域
 103 : 第3の過程が行われる領域
 104 : UV/O₃照射ランプ
 105 : UV照射ランプ
 111、119 : ストッカー
 112 : 搬送機
 118 : ハンドラー
 113、120 : ベルトコンベアー
 114 : 補助ローラ
 121 : 送りローラ
 115 : 印字用トレー
 116 : ポンプ
 117 : 送りモーター
 130Y、130M、130C、130B : インクの各色 (Y、M、C、B) 及び記録ヘッド
 211 : スペーサー
 401 : 被記録媒体
 402 : 温度センサー
 403 : モーター
 410 : 記録ヘッド
 501 : 基紙
 503 : インク受容層

505 : 多孔質微粒子
 507 : 接着剤
 509 : インク浸透部
 601 : 被記録媒体
 602 : 架橋ポリマー
 603 : 微粒子
 605 : 色材
 607 : 微粒子の凝集物
 609 : 主画像部IM内の被記録媒体表面近傍の微粒子
 10 の凝集物
 I : 着色部
 IM : 主画像部
 IS : 主画像部の周辺部
 701 : インクと液体組成物の反応物
 702 : 液体組成物との反応に関与しなかったインク
 703 : 被記録媒体
 704 : 色材
 705 : モノマー
 706 : 液体組成物
 20 707 : 液体組成物の液溜り
 709 : 被記録媒体表面近傍の微粒子
 711 : 微粒子の凝集物
 713 : インク
 716 : 付与される外部エネルギー

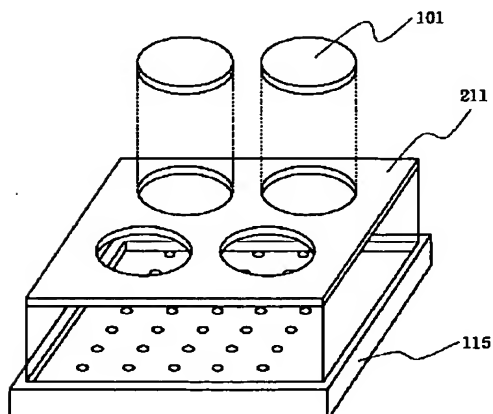
【図1】



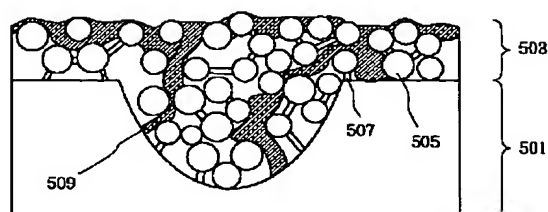
【図2】



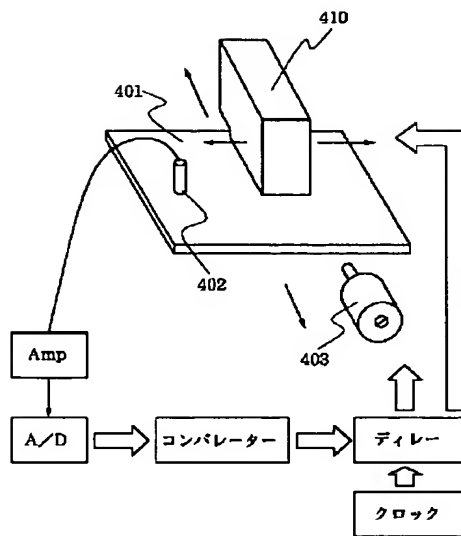
【図3】



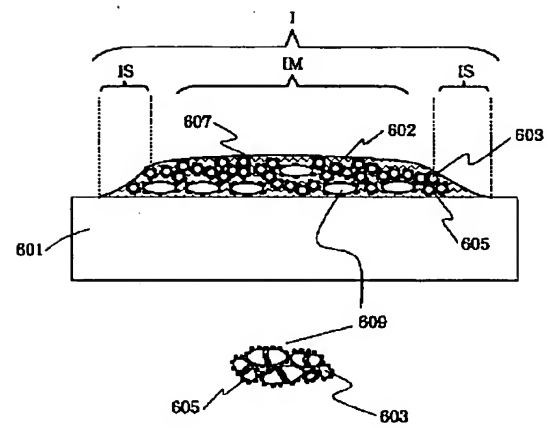
【図5】



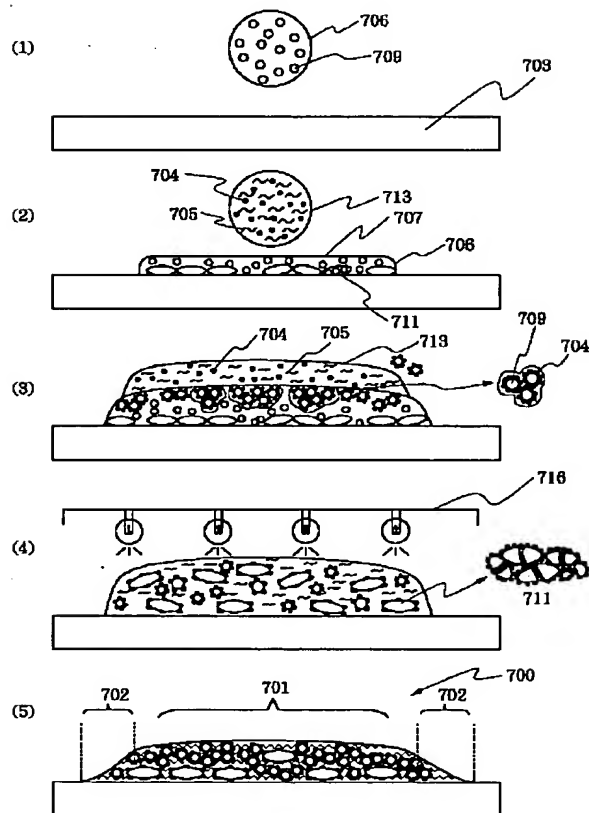
【図 4】



【図 6】



【図 7】



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Fターム(参考) 2C056 EA04 FA03 FC01 FD05
2H086 BA01 BA53 BA55
4J039 BE01 BE06 BE27 EA03 EA06
EA08 EA15 EA16 EA17 EA19
EA20 EA34 EA36 EA41 EA42
EA44 GA24

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